ELEMENTARY

ORGANIC CHEMISTRY

BY

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PREFACE TO THE THIRD EDITION.

In view of the suggestions from many colleagues and friends, the book has been thoroughly revised and practically rewritten. The chapters have been rearranged and additional matter added. Many more experiments have been included and diagrams introduced.

I believe that the book will be found more useful by the students for whom it is meant.

My thanks are due to all my colleagues who have been giving valuable suggestions from time to time and also to Mr. Shyam Narain Bhargava, B. Sc., for the additional diagrams and Mr. Prabhu Lal, one of my pupils, for helping me in correcting the proofs.

Maharaja's College Hostel,
Jaipur.
25th Feb. 1938

C. L. M.

CONTENTS.

APPENDICES.

CHAPTER I.

INTRODUCTORY

The study of chemistry is not limited to substances of atmospheric or mineral origins only. Substances contained in or obtained from plant or animal bodies are also included in this study because they also are material things.

Substances of animal or vegetable origin could not be synthesised in the laboratory till 1828. It was naturally a common belief that such substances could only be formed under the influence of *life* (a term more expressive of ignorance than knowledge of the phenomenon under consideration). It was known that these substances possessed certain properties which were not ordinarily found in substances of mineral origin The name **Organic** was given to such substances to distinguish them from substances of mineral origin which were named as **Inorganic.**

In the year 1828 Wöhler accidentally obtained urea (a substance contained in the urine of carnivorous mammals and birds) from inorganic substances. This substance till then was not synthesised in the laboratory. Afterwards some other substances

which were classed as organic were synthesised. Therefore the then existing distinction between the organic and inorganic chemistry was abandoned

It was already known that all substances which were classed as organic contained the element carbon as their common constituent. Therefore **Organic chemistry,** since then, **is the chemistry of carbon compounds.**

The idea of entirely giving up the distinction between these two branches of chemistry might occur to the student as a natural consequence but the distinction is still retained mainly for two reasons :—

1. The number of organic substances is enormously large and additions are being made every year to the existing list. It would, therefore, be inconvenient to study them along with inorganic compounds.

2. Organic substances have got some perculiarities of their own. (see appendix A)

CHAPTER II.

WOOD DISTILLATION

To study organic chemistry it appears to be natural to start with a substance of plant or animal origin. Wood may be taken as a convenient natural substance to start with.

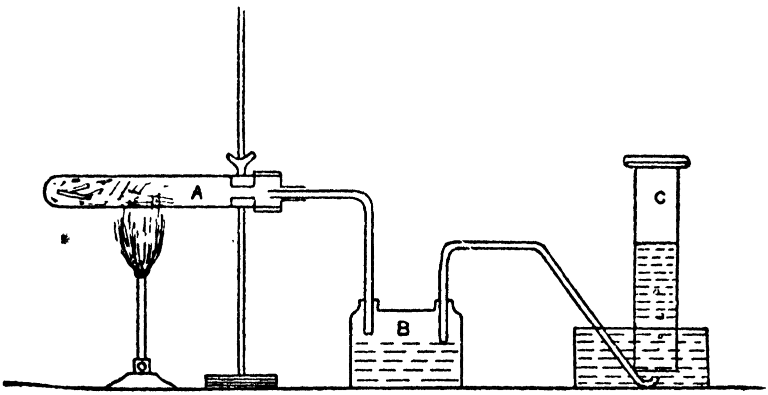

Fig. 1.

When a substance is heated out of contact with air so that it breaks up into a number of constituents without being burnt or oxidised, and the constituents are condensed by suitable means, it is said to have undergone **destructive distillation.** If wood is subjected to such a distillation, the following important products are obtained :

1. Inflammable gases;
2. Pyroligneous acid (an acid liquid);
3. Tar (a thick sticky liquid);
4. Wood charcoal (solid residue in the vessel).

Experiment 1. Fit up an apparatus as shown in figure 1. In the copper tube *A* take some small pieces of ordinary wood and heat. Put a little water in the bottle *B*. After heating the metal tube for some time, it will be observed that a dark liquid has settled down at the bottom of *B* and if the liquid in this bottle is tested with litmus paper it will be found to be acidic. The gas collected in the cylinder *C* will burn. The metal tube will be found to contain charcoal.

The following are the main constituents of pyroligneous acid :—

1. Acetic acid;
2. Wood Spirit (methyl alcohol);
3. Acetone.

Before they can be studied they must be separated from each other. In pyroligneous acid there are three liquids which are miscible. If out of these three liquids one can be converted into a stable non-volatile solid, it can be separated from the other two liquids by distillation. This can be accomplished by treating the acid distillate with lime. Only Acetic acid will react with lime and will be converted into calcium acetate (action of a base with an acid). Now if this mixture is distilled the distillate will contain mythyl alcohol and acetone, while calcium acetate will remain in the distilling vessel as a solid residue.

Isolation and Purification of Acetic Acid.

Calcium acetate obtained as above is distilled with conc. sulphuric acid (action of a *strong* acid on the salt of a *weak* acid). Acetic acid being volatile, will distill over. This acid is impure because it has been obtained from impure calcium acetate. **A substance can easily be purified if it can easily be crystallised.** Sodium acetate can easily be crystallised, therefore the impure acid is converted into sodium acetate by treatment with sodium carbonate and this is purified by repeated recrystallisation. Sodium acetate contains two molecules of water of crystallisation. It is heated in an iron basin to get rid of this water. Anhydrous pure sodium acetate is thus obtained which is distilled with pure conc. sulphuric acid. The distillate is pure acetic acid which is also known as **glacial acetic acid** because at low temperatures it crystallises out having snow like appearance.

Separation and Purification of Methyl Alcohol.

Boiling point of methyl alcohol is 66°C and that of acetone is 56°C. Although their boiling points are not far apart, yet **Fractional Distillation** is the only commercial means of their separation. (See appendix F). The liquids obtained in this way are not pure. Methyl alcohol contains acetone, and acetone contains methyl alcohol.

To get methyl alcohol free from acetone, the commercial alcohol is treated with fused calcium

chloride which takes up methyl alcohol as **alcohol of crystallisation** and crystallises out. These crystals are separated and dried at low temperature. They are then subjected to distillation whereby methyl alcohol distills over leaving calcium chloride in the distilling vessel.

Methyl alcohol is manufactured from wood and is known as **wood spirit.** Unless it is chemically purified it always contains acetone.

Analysis of Methyl Alcohol.

When methyl alcohol is analysed qualitatively (see Appendix C), it is found to contain carbon, hydrogen, and oxygen. The quantitative analysis (see Appendix D) shows that its empirical formula should be CH_4O. Vapour density determination (see Appendix E) shows that the molecular weight is 32 which indicates the identity of the empirical and molecular formulæ.

CHAPTER III.

FERMENTATION

Isolation of Ethyl Alcohol

When Brewer's Yeast* (a little *Khamir* from the baker will do) is added to a solution of grape sugar ($C_6H_{12}O_6$) and left alone for a few days, it is observed that the solution acquires intoxicating properties and that carbon dioxide is given out. Owing to the evolution of carbon dioxide the solution appears as if it is boiling although there is no appreciable rise in temperature. This process is known as **alcoholic fermentation.**

Experiment 2. Take some grape sugar solution in the conical flask and add to it a little Khamir Leave it alone for two or three days in a warm place The liquid will begin to froth and the lime water in the cylinder will turn milky. . Distil the liquid contained in the flask and test for ethyl alcohol.

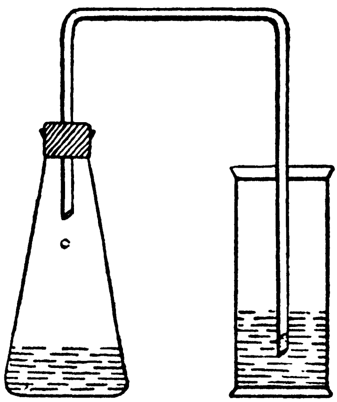

Fig. 2.

* Brewer's yeast is a culture preparation which contains a very large number of microscopically small unicellular organisms called yeast cells.

To obtain alcohol from this fermented liquid, it is first subjected to fractional distillation **(Rectification)** whereby a solution containing from 90 to 95% of alcohol is obtained. This alcohol is commercially known as **Rectified Spirit of Wine.** To further dehydrate it, it is distilled twice or thrice over quicklime (calcium oxide). In this way alcohol of about 98% strength can be obtained. To remove the last traces of water from alcohol it is left in contact with a little more than the theoretical quantity of metallic calcium or sodium and distilled. This anhydrous alcohol is known as **Absolute Alcohol.** It is very hydroscopic. Chemically this substance is known as **Ethyl Alcohol.**

Theory of the Mechanism of Fermentation.

Without yeast there is no fermentation. Therefore yeast is the medium of fermentation. When yeast is boiled before it is added to the sugar solution, there is again no fermentation; therefore the natural inference is that when boiled, the yeast cells die and it is only the living cells which can bring about fermentation or it is the life in yeast plant which in some way or the other is connected with fermentation

But when yeast after being crushed with kieslguhr (a siliceous earth) was subjected to a very high pressure (Buchner, 1897) and a juice was extracted by suitable means and it was examined free from

yeast cells, it was found capable of bringing about fermentation. Now the natural consequence is that the yeast cells give out some substance which works like a catalytic agent and can bring about alcoholic fermentation.

Some other changes were observed which are brought about by microscopic organisms and it is believed that like yeast these organisms produce substances of which it is the specific property to bring about these chemical changes. These substances are known by the name of **enzymes** or **ferments.** The enzyme which is given out by yeast and which brings about alcoholic fermentation is called **zymase**.

If instead of using grape sugar, a solution of ordinary sugar (cane sugar) is employed, the fermentation is delayed for some time. The reason is that cane sugar as such cannot be fermented by zymase. It is converted into a mixture of grape and fruit sugars by another enzyme, **invertase**, which is invariably associated with yeast cells, and it is after **inversion** that fermentation starts.

Alcoholic Drinks.

All alcoholic drinks contain ethyl alcohol as their active intoxicating constituent. The percentage of alcohol differs in different liquors. They are all prepared by fermentation.

Beer is an alcoholic drink containing from 3 to 6 per cent alcohol. It is prepared from barley, which

is soaked in water and is kept at a suitable temperature to allow *germination* to proceed. During germination enzymy **diastase** is formed in the seeds, which is capable of converting insoluble starch into soluble *maltose* and *dextrin* After some time the seeds are heated to stop germination and to cause the production of certain substances which impart the necessary flavour and colour to the product The dried seeds are known as **malt**, which is steeped in water and left alone for some time when the diastase converts starch into maltose and dextrin. The liquid, **wort,** is now boiled with **hops** (dried flowers of hop plant) which acts as an antiseptic or preservative and imparts a slightly bitter taste. The boiled liquid is cooled and yeast is added to start fermentation. Maltose undergoes alcoholic fermentation in the same way as cane sugar. The quantity of maltose being very small only a small proportion of alcohol is formed. If a larger quantity of alcohol is required, some grape sugar is added to the fermenting liquid. After the fermentation has stopped, the liquor is run into casks and left alone for some time to "brighten" before it is ready for the market. The wort is incapable of resisting the action of certain other organisms which are always present in the atmosphere, and which set in other fermentations and spoil the drink. Therefore scrupulous cleanliness is always observed in the brewing of beer.

Wines are obtained from grape juice which con-

tains grape sugar and fruit sugar. The fermentation starts spontaneously because yeast cells are always present in grapes and their stalks and also in air. External addition of yeast is not necessary in the preparation of wines. The natural acidity of the grape juice does not allow the other organisms to react.

Whisky is obtained by distilling a fermented solution of malt. It contains about 40% alcohol.

Brandy is prepared by the distillation of wines. It contains about 50% of alcohol.

In India cheap liquors are obtained by the fermentation of Molasses (*Sheera*) and *Mahua* (महुआ). **Toddy** (ताड़ी) is a drink which is prepared by fermenting the juice obtained from the trunk of the palm tree.

In some Indian States specially in Jaipur liquors of high quality were prepared by making use of spices and dry fruits. The industry is now declining.

Physiological action of alcohol. If alcohol is taken in small quantities it works as a stimulent and is a valuable drug, but in larger quantities it works as an intoxicant and has a poisonous effect on the nerves and reduces the resisting power of the body to various diseases.

To restrict the consumption of alcoholic drinks, a heavy excise duty is levied on all alcoholic preparations which can be used as intoxicants.

Manufacture of ethyl alcohol. Alcohol is manufactured by the fermentation of molasses, starchy substances (*e. g.* potatoes, barley, corn and rice) and Mahua fruits. The substance is allowed to ferment with yeast in large wooden tanks and when the fermentation is complete, it is subjected to fractional distillation (rectification) to obtain rectified spirit.

Methylated Spirit is ethyl alcohol mixed with methyl alcohol (wood spirit) and some other substances (the Indian Excise Department uses pyridine for this purpose) which render it incapable of being taken internally, and is sold duty free. It is largely used in the preparation of varnishes, in stoves and also in some other industries.

Alcoholometry. Percentage of ethyl alcohol in aqueous solutions is determined by the help of the specific gravity of the solution. Solutions of different strengths have different densities. Tables showing the relation of specific gravity and strength are prepared from solutions of known strength and it is by reference to these tables that the strength of an unknown solution of alcohol is determined.

An alcoholic liquor containing 49·3% alcohol by weight or 57·09% by volume at 51°F is known as "proof spirit." Other solutions are known as *over proof* or *under proof* according as the percentage of alcohol is higher or lower.

Owing to the presence of foreign substances in most of the alcoholic drinks, the strength of alcohol

cannot be determined by the direct measurement of specific gravity. A known volume of the liquor is taken in a distilling flask and the major portion of the liquid is distilled. The distillate is made up to the original volume with water and the specific gravity determined.

Analysis of Ethyl Alcohol. The qualitative analysis of ethyl alcohol shows that like methyl alcohol, it also contains the elements carbon hydrogen, and oxygen. The gravimetric analysis shows that the simplest formula should be C_2H_6O. The vapour density is found to be 23 which gives the molecular weight to be 46 showing thereby that the empirical and molecular formulae are identical.

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CHAPTER IV.

SOME PROPERTIES OF METHYL AND ETHYL ALCOHOLS

Physical Properties.

Both the substances are colourless, mobile liquids, miscible with water in all proportions. They have their own characteristic vinous odour. Methyl alcohol boils at 66°C, while ethyl alcohol boils at 78°C. They are lighter than water.

Chemical Properties.

1. Both of them burn with a non-luminous flame forming carbon dioxide and water.

$$2CH_4O + 3O_2 = 2CO_2 + 4H_2O.$$
$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O.$$

2. Like water both the alcohols evolve hydrogen when treated with metallic sodium or potassium.

$$2CH_4O + 2Na = 2CH_3{\cdot}ONa + H_2.$$
$$2C_2H_6O + 2Na = 2C_2H_5{\cdot}ONa + H_2.$$

3. With phosphorous pentachloride (PCl_5) they evolve hydrogen chloride and the alcohol is converted into a monochloro derivative in which the chlorine atom takes the place of one atom of hydrogen and one atom of oxygen.

$$CH_4O + PCl_5 = CH_3Cl + POCl_3 + HCl.$$
$$C_2H_6O + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

In this reaction also, methyl and ethyl alcohols resemble water.

$$H_2O + PCl_5 = HCl + POCl_3 + HCl.$$

4. Towards acids they behave like caustic soda.

$$NaOH + HCl = NaCl + H_2O.$$
$$CH_4O + HCl = CH_3Cl + H_2O.$$
$$C_2H_6O + HCl = C\ H_5Cl + H_2O.$$

and

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O.$$
$$CH_4O + H_2SO_4 = CH_3HSO_4 + H_2O.$$
$$C_2H_6O + H_2SO_4 = C_2H_5HSO_4 + H_2O$$

In all the above reactions it will be observed that **the groups —CH_3 and —C_2H_5 play the same part as an atom of hydrogen in water or that of sodium in caustic soda**. Such **monovalent** radicals or groups of atoms with the general formula C_nH_{2n+1} are known by the name of **alkyl groups**. The —CH_3 group is called as the **methyl group** while the —C_2H_5 group is known as the **ethyl group** or radical.

Homologous Series. When we compare the molecular formulae of methyl and ethyl alcohols, we find that there is a difference of CH_2 between the two formulae. An alcohol is known which differs from ethyl alcohol by CH_2 in the same way as ethyl alcohol differs from methyl alcohol. This is known as propyl alcohol (C_3H_8O). Similarly other higher

alcohols are also known which differ from member to member by CH_2. They resemble one another in their chemical properties like the two alcohols mentioned above. Such **a series of compounds which belong to the same class and which differ from one another by CH_2 is known as a Homologous Series and the members are known as Homologues.**

EXERCISES ON CHAPTERS I—IV.

1. What do you understand by the term "Organic Chemistry"?

2. What are the main reasons for which the carbon compounds are studied separately from the compounds of other elements?

3. What are the main products of the destructive distillation of of wood? How will you obtain a pure sample of (*a*) acetic acid and (*b*) methyl alcohol from the above products?

4. How will you detect the presence of Carbon, Hydrogen, Nitrogen, Chlorine, and sulphur in a given organic compound?

5. Give the chemical principles involved in the estimation of different elements in organic compounds.

6. What are Enzymes? How do enzymes react?

7. What is Fermentation? Illustrate your answer with reference to the alcoholic fermentation of grape sugar.

8. Explain the following terms giving examples :—

(*a*) Homologous Series, (*b*) Rectificed Spirit, (*c*) Rectification, (*d*) Destructive Distillation, (*e*) Fractional Distillation, and (*f*) Alkyl Group.

9. Write down equations to illustrate the action of Na, PCl_5, H_2SO_4 and HCl on methyl and ethyl alcohols.

10 How is ethyl alcohol prepared on a large scale? Mention the various raw materials used and briefly state the changes involved in their conversion into alcohol.

11. How will you prepare pure samples of ethyl alcohol and acetic acid from a mixture of these two liquids?

CHAPTER V.

HYDROCARBONS

Hydrocarbons are compounds which contain the elements carbon and hydrogen only.

They may be classified as follows :—

Hydrocarbons

- Aliphatic or Open Chain
  - Saturated (*e.g.*, CH_4, C_2H_6) General formula C_nH_{2n+2}
  - Unsaturated
    - Olefines (*e.g.*, C_2H_4) General formula C_nH_{2n}
    - Acetylenes (*e.g.*, C_2H_2). General formula C_nH_{2n-2}
- Closed Chain (these are further classified but only benzene will be considered in this book)

It has been found that carbon atoms have got the peculiarity of combining with one another to form open or closed chains of carbon atoms. Those hydrocarbons which contain an open chain of carbon atoms are known as **Aliphatic Hydrocarbons** or the hydrocarbons of the Methane Series—Methane (CH_4)

being the simplest member containing only one carbon atom.

Petroleum is the chief source of the hydrocarbons of this series.

METHANE, *marsh gas*, (CH_4).

Methane is given out as exhalation from the earth in petroleum areas. It also occurs as *fire damp* in mines and as *marsh gas* in marshy areas.

Preparation. 1. When anhydrous sodium acetate is heated with soda lime, methane is evolved.

$$CH_3|\underline{\overline{CO.ONa + NaO}}|H = CH_4 + Na_2CO_3.$$

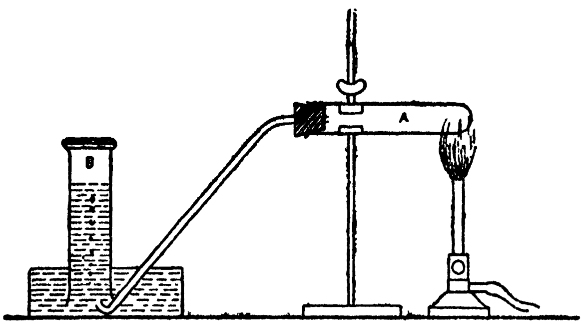


Fig. 3.

Experiment 3. Fit up an apparatus as shown in the figure. In the metal or hard glass tube *A* take a well powdered mixture of sodium acetate (anhydrous) and soda lime. Heat the tube strongly, Methane will be evolved which being an insoluble gas can be collected over water as shown in the figure.

2. Methane may also be obtained by the reduction of methyl chloride, bromide, or iodide with nascent hydrogen produced by the action of zinc-copper couple on alcohol or water, or aluminium-mercury couple on methyl alcohol.

$$CH_3\boxed{I + H}H = CH_4 + HI.$$

3. Methane is produced when a mixture of hydrogen sulphide and vapours of carbon bisulphide are passed over heated copper turnings.

$$2H_2S + CS_2 + 8Cu = 4Cu_2S + CH_4.$$

4. Pure methane is obtained by the action of water on aluminium carbide.

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

Properties. Methane is a colourless and odourless gas. It is insoluble in water but dissolves readily in alcohol.

It burns with a pale luminous flame and forms an explosive mixture with air or oxygen.

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

The fire-damp explosions of mines are due to the explosions of mixtures of methane and oxygen.

Electric sparks decompose methane into its elements.

It resists the action of most of the oxidising and reducing agents as also of the caustic alkalies and conc. sulphuric and nitric acids.

Chlorine and bromine react with methane replacing one or more atoms of hydrogen by the halogen and evolving the ***hydracid*** of the halogen.

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$
$$CH_3Cl + Cl_2 = CH_2Cl_2 + HCl.$$
$$CH_2Cl_2 + Cl_2 = CHCl_3 + HCl.$$
$$CHCl_3 + Cl_2 = CCl_4 + HCl.$$

This process is known as **substitution.** When the halogen derivative of a hydrocarbon is converted into the hydrocarbon by reduction, the change is known as **inverse substitution.** Thus, the conversion of methane into methyl chloride etc., is substitution while the reverse change *i. e.*, the conversion of methyl chloride etc. into methane is inverse substitution.

Iodine does not bring about substitution because hydriodic acid is produced in the reaction which being unstable works as a reducing agent and brings about inverse substitution. Iodine substitution products are prepared indirectly.

ETHANE (C_2H_6).

Ethane is the next higher homologue of methane.

Preparation. 1. Like methane it may be prepared by heating dry sodium propionate $C_2H_5 \cdot CO.ONa$ (sodium salt of propionic acid which is the next higher homologue of acetic acid) with soda lime.

$$C_2H_5 \cdot \boxed{CO.ONa + NaO}H = C_2H_6 + Na_2CO_3.$$

2. Ethane may also be prepared by the inverse substitution of the halogen derivatives of ethane (*e.g.*, ethyl chloride, bromide or iodide).

$$C_2H_5\,\boxed{I+H}\,H = C_2H_6 + HI.$$

3. When potassium acetate ($CH_3.CO.OK$) is electrolysed under suitable conditions ethane is evolved at the anode.

Potassium acetate ionises as follow :—

$$CH_3.CO.OK \rightleftarrows K^{\cdot} + (CH_3.CO.O)'$$

When the negative ions $(C_2H_3O_2)'$ reach the anode they discharge their electricity and being unstable they decompose immediately into $—CH_3$ and CO_2. Two $—CH_3$ groups join together to form a molecule of ethane C_2H_6.

4. When methyl chloride, bromide or iodide is treated with metallic sodium or zinc, ethane is produced.

$$2CH_3I + Zn = C_2H_6 + ZnI_2.$$

$$2CH_3Cl + 2Na = C_2H_6 + 2NaCl.$$

This reaction throws some light on the arrangement of atoms in the molecule of ethane. If the valency of carbon is taken to be four it appears that in methyl chloride one of the valencies of the carbon atom is occupied by the chlorine atom. Now chlorine having a great affinity for zinc or sodium leaves the methyl groups which join in pairs to form molecules of ethane. This shows that in ethane the two carbon atoms are joined together by

a single valency. This change may be represented thus :—

$$
\begin{array}{c} H \\ | \\ H-C- \\ | \\ H \end{array}
\boxed{\begin{array}{c} Cl+Cl \\ + \\ Zn \end{array}}
\begin{array}{c} H \\ | \\ -C-H \\ | \\ H \end{array}
=
\begin{array}{c} H \quad H \\ | \quad\; | \\ H-C-C-H \\ | \quad\; | \\ H \quad H \end{array}
+ ZnCl_2.
$$

Properties. Ethane is a colourless and odourless gas. It does not dissolve in water and is slightly soluble in alcohol. Like methane it resists the action of oxidising and reducing agents, sulphuric acid, and caustic alkalies.

It burns with a luminous flame and forms an explosive mixture with air and oxygen.

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O.$$

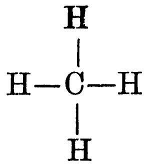
Like methane it reacts with chlorine and bromine to form substitution products. The final products being C_2Cl_6 and C_2Br_6 (hexachloro—and hexabromo—ethane.)

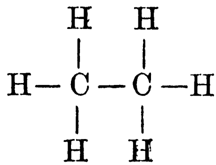
As has been mentioned above in most of its properties, ethane closely resembles methane.

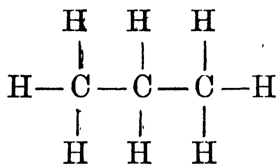
Other Homologues of Methane.

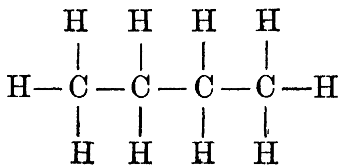
Hydrocarbons are known which contain more than two carbon atoms and of which the methods of formation and properties are similar to those of methane and ethane. They may be regarded as having been formed by the combination of carbon atoms in

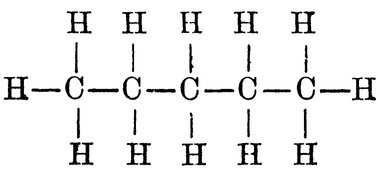
chains, the remaining valencies of the carbon atoms being satisfied by hydrogen atoms. The following are only a few of the examples of such a series of hydrocarbons which together are known by the name of **Saturated Hydrocarbons** or **Paraffins.**

1.  Methane (CH_4)

2.  Ethane (C_2H_6)

3.  Propane (C_3H_8)

4.  Butane (C_4H_{10})

5.  Pentane (C_5H_{12})

The general formula C_nH_{2n+2} of this homologous series of paraffins will be quite clear with a little reflection over these **graphical formulae.**

OLEFINES C_nH_{2n}

ETHYLENE (C_2H_4).

Ethylene is a hydrocarbon which contains less hydrogen than the saturated hydrocarbon containing the same number of carbon atoms (ethane.)

Preparation. 1. Ethylene is prepared in the laboratory by heating ethyl alcohol with excess of concentrated sulphuric acid at about 165°C. Sulphur dioxide is always produced in this reaction owing to the reduction of some sulphuric acid by alcohol. To avoid the presence of sulphur dioxide syrupy (ortho) phosphoric acid is sometimes advantageously used.

$$C_2H_6O = C_2H_4 + H_2O$$

Phosphoric and sulphuric acids *probably* work as dehydrating agents.

Experiment 4. Fit up an apparatus as shown in figure 4. In the flask take some (25 c. c.) syrupy phosphoric acid or conc. sulphuric acid. Put some ethyl alcohol in the dropping funnel. Heat the flask on sand bath till the temperature reaches 165°C and drop the alcohol from the dropping funnel. Ethylene will be formed and may be collected over water as shown in the figure. If sulphuric acid is used, the gas may be purified by passing through caustic potash which will absorb sulphur dioxide.

2. Ethylene may be prepared by heating ethyl chloride, bromide or iodide with *alcoholic* caustic potash. The reaction may be represented thus.

(1) $C_2H_5Cl = HCl + C_2H_4.$

(2) $HCl + KOH = KCl + H_2O$.

adding (1) and (2)

$$C_2H_5Cl + KOH = C_2H_4 + KCl + H_2O.$$

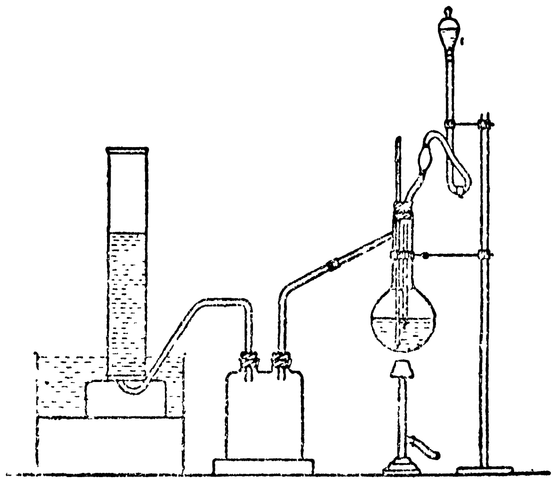


Fig. 4.

Properties. Ethylene is a colourless gas with a peculiar sweet odour. It is sparingly soluble in water but soluble in ether and alcohol. It burns with a luminous flame and forms an explosive mixture with air or oxygen.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

Ethylene combines directly with hydrogen at high temperatures forming ethane. If the reaction is to be carried on at low temperatures a catalytic agent (platinum black or finely divided nickel) should be used.

$$C_2H_4 + H_2 = C_2H_6 \text{ (ethane)}$$

It also combines directly with hydrogen bromide, hydrogen iodide, bromine, chlorine, and iodine.

$$C_2H_4 + HBr = C_2H_5Br. \text{ (ethyl bromide)}$$
$$C_2H_4 + HI = C_2H_5I \text{ (ethyl iodide)}$$
$$C_2H_4 + Br_2 = C_2H_4Br_2 \text{ (ethylene dibromide)}$$
$$C_2H_4 + Cl_2 = C_2H_4Cl_2 \text{ (ethylene dichloride)}$$
$$C_2H_4 + I_2 = C_2H_4I_2 \text{ (ethylene di-iodide)}$$

When it is passed through *fuming* sulphuric acid, it is absorbed and combines with sulphuric acid to form ethyl hydrogen sulphate.

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4 \text{ (ethyl hydrogen sulphate)}$$

A dilute solution of alkaline permanganate is decolourised (see *ethylene glycol*).

Uses. Ethylene is present in the illuminating gas and has recently been applied as an anaesthetic. Over chloroform it has the advantage of not producing unpleasant after-effects.

Saturated and Unsaturated Compounds. In contrast to the action of chlorine, bromine and iodine on methane and ethane, it is observed that ethylene forms compounds by direct addition. It is for this reason that ethylene is known as an **unsaturated** hydrocarbon. Those compounds which do not form other compounds by direct addition are called **saturated.** They form compounds by substitution.

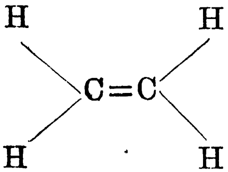
Constitution of Ethylene. After the determina-

tion of the molecular formula of a compound, it is necessary to try to find out the probable arrangement of atoms in the molecule of the substance.

1. The molecular formula of ethylene is found to be C_2H_4.

2. As the compound contains only carbon and hydrogen and as hydrogen is monovalent, the two carbon atoms must be directly joined together.

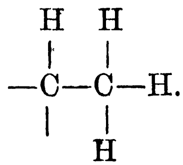
3. Taking the valency of carbon to be four and that of hydrogen to be one, the following two alternative formulæ are possible :



(1)

(symmetrical)

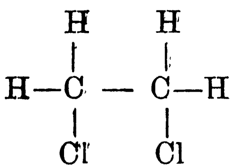
and



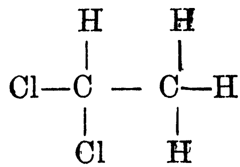
(2)

(unsymmetrical)

4. Ethylene, when treated with chlorine, gives an addition product with the molecular formula $C_2H_4Cl_2$ which should be represented as



or



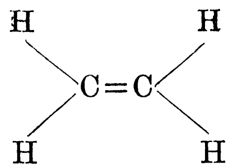
according as ethylene is symmetrical (1) or unsymmetrical (2).

Actually two such dichloro ethanes are known. The unsymmetrical compound is obtained from acetaldehyde and is in accordance with the consti-

tution of acetaldehyde (see acetaldehyde) and is different from that which is obtained from ethylene.

5. This shows that ethylene should be represented by the formula No. (1) *i. e.*, the symmetrical formula.

It is believed that there is a double bond between the two atoms of carbon contained in the molecule of ethylene.



It might be supposed that the double bond between the two carbon atoms should increase the stability of the compound. But the facts are quite contrary to this idea. **The double bond is a sign of weakness and during chemical changes it is at this point that the molecule breaks.** It is for this reason that unsaturated compounds form **addition products.**

Other Homologues of Ethylene. Ethylene is the first member of the homologous series of compounds which are known by the name of **olefines**. Propylene (C_3H_6) and butylene (C_4H_8) are the second and third members of the series. The general formula of these hydrocarbons is C_nH_{2n} *i. e.*, they contain two atoms of hydrogen less than the corresponding paraffins or saturated hydrocarbons. The hydrocarbon methylene, containing only one carbon atom (CH_2) is unknown.

ACETYLENES. C_nH_{2n-2}

There is another class of unsaturated hydrocarbons called **acetylenes.** They contain four hydrogen atoms less than the corresponding saturated hydrocarbons. The general formula should, therefore, be C_nH_{2n-2}

ACETYLENE. (C_2H_2.)

Acetylene is the first member of the series. In small quantities it is present in coal gas.

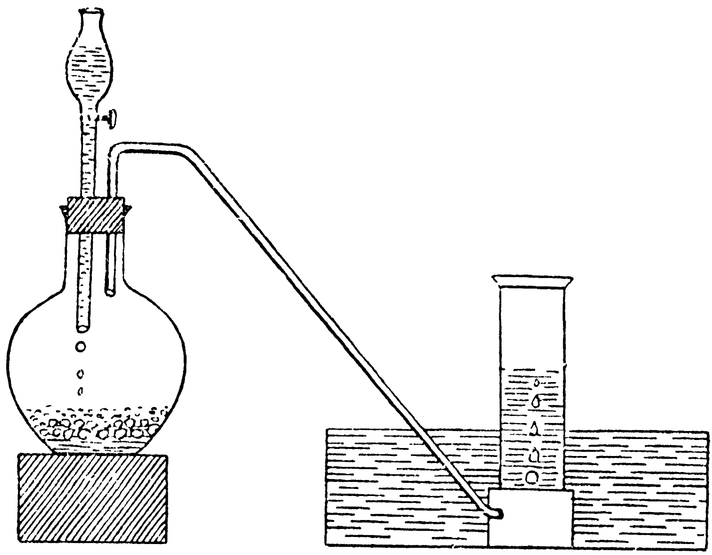


Fig. 5.

Preparation 1. Acetylene is prepared by the action of water on calcium carbide (CaC_2).

$$CaC_2 + 2H_2O = C_2H_2 + Ca\,(OH)_2.$$

Experiment 5. Fit up an apparatus as shown in the figure Put calcium carbide over a layer of sand in the flask and let water

flow from the dropping funnel in a very gentle stream. The gas may be collected over water as shown in the figure.

2. Acetylene may be obtained in small quantities by passing electric sparks between two carbon poles in an atmosphere of hydrogen.

Fig. 6

3 It may also be obtained by the action o *alcoholic* caustic potash on ethylene dibromide ($C_2H_4Br_2$).

1. $C_2H_4Br_2 = C_2H_2 + 2HBr$.
2. $2HBr + 2KOH = 2KBr + 2H_2O$.

adding,

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

This reaction is analogous to the action of alcoholic caustic potash on ethyl bromide when ethylene is formed.

Properties. Acetylene is a colourless gas with a peculiar unpleasant garlic odour. Water dissolves its own volume of acetylene. It is very soluble in acetone and the solution is used as a source of acetylene on industrial scale. It is poisonous.

It burns with a very smoky luminous flame. But it has a very high illuminating power when it is allowed to burn at a small jet. Under these conditions its flame is non-smoky.

Like methane, ethane, and ethylene, it also forms an explosive mixture with air or oxygen.

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O.$$

Like ethylene it forms additive compounds with halogens and some other reagents :—

(*a*) Hydrogen gives first ethylene and finally ethane.

$$C_2H_2 + H_2 = C_2H_4 \text{ (ethylene)}$$
$$C_2H_4 + H_2 = C_2H_6 \text{ (ethane).}$$

These reactions take place in the presence of catalytic agents, *e. g.*, finely divided nickel or platinum black.

(*b*) With halogens acetylene forms first dihalides and finally tetrahalides.

$$C_2H_2 + Br_2 = C_2H_2Br_2 \text{ (dibromo } \textit{ethylene}\text{)}$$
$$C_2H_2Br_2 + Br_2 = C_2H_2Br_4 \text{ (tetrabromo } \textit{ethane}\text{).}$$

(*c*) Acetylene combines with hydrogen bromide and iodide.

$C_2H_2 + HI = C_2H_3I.$ Mono-iodo-*ethylene*

$C_2H_3I + HI = C_2H_4I_2.$ *Ethylidene* di-iodide

Oxidised with chromic acid (H_2CrO_4 or Cr_2O_3) acetylene gives acetic acid.

$$C_2H_2 + O + H_2O = CH_3{\cdot}COOH. \text{ (acetic acid)}$$

Potassium permanganate oxidises acetylene to oxalic acid.

$C_2H_2 + 4O = C_2H_2O_4$ (oxalic acid).

When acetylene is passed through a red hot tube, it changes into benzene (C_6H_6).

$3C_2H_2 = C_6H_6$ (benzene).

Three molecules of acetylene combine together to form a molecule of benzene. Such **a change where two or more molecules of a compound combine together to form one molecule of another substance is known as polymerisation.** The polymer should be reconvertable into the original substance (See aldehydes).

Acetylene can easily be distinguished from ethylene, methane and ethane etc., by its smell and also by its action on an ammoniacal solution of cuprous chloride with which it forms a red precipitate of copper acetylide ($C_2Cu_2.H_2O$). Similarly with an ammoniacal solution of silver nitrate, acetylene gives silver acetylide ($C_2Ag_2.H_2O$) which is a white amorphous powder. The silver compound is more violently explosive than the copper acetylide.

Uses. Owing to its high illuminating power, it is used as an illuminant and also in oxy-acetylene flames in steel moulding where a high temperature is required.

Comparison of the Properties of Methane, Ethylene and Acetylene.

	Methane.	Ethylene.	Acetylene.
1. Formula.	CH_4.	C_2H_4	C_2H_2.
2. State.	Gas.	Gas.	Gas.
3. Colour.	Colourless.	Colourless.	Colourless.
4 Combustibility.	Burns with pale blue flame.	Burns with luminous flame.	Burns with luminous smoky flame.
5. Solubility. in water.	Insoluble.	Sparingly soluble.	Sparingly soluble.
6. Action of chlorine, bromine.	Forms substitution products $CH_4 + Cl_2 = CH_3Cl + HCl$.	Forms addition products $C_2H_4 + Cl_2 = C_2H_4Cl_2$	Forms addition products $C_2H_2 + 2Cl_2 = C_2H_2Cl_4$.
7. Action of HBr, and HI.	No action.	Forms addition products $C_2H_4 + HBr = C_2H_5Br$.	Forms addition products $C_2H_2 + 2HBr = C_2H_4Br_2$.
8. Action of sulphuric acid.	No action.	Forms ethyl hydrogen sulphate.	Acetaldehyde is produced if solution of gas is added to water.
9. Action of ammoniacal cuprous chloride.	No action.	No action.	Forms red ppt. of copper acetylide ($C_2Cu_2.H_2O$).

Paraffin or Petroleum Industry. It was mentioned in the beginning of this chapter that petroleum is the source of a very large number of Saturated Hydrocarbons (Paraffins) which are of great commercial importance.

Crude petroleum which is also known as earth oil, rock oil or mineral oil, occurs in different parts of the world in the form of oily deposits. The chief sources of the oil are :

1. America where it was first discovered in 1859 by Colonel Drake ;
2. Baku district near the Caspian sea in Russia ;
3. Burmah.

In India the Attock Oil Company have recently explored the oil fields of the Attock District in the Punjab and have bored a large number of wells. The Oil is taken to Rawalpindi by pipe lines where they have erected refinery and storage tanks.

The **origin of petroleum** is attributed to the following two causes :—

1. It is produced by the action of water on the iron carbides contained in the subterranian mineral deposits, in the same way as methane is obtained by the action of water on aluminium carbide.

2. It is formed by the decomposition of the remains of marine animals under high temperature and pressure obtained in the earth's crust.

At the refineries the crude oil is fractionally distilled and divided into the following fractions according to their boiling points.

Fraction.	Range of temp.	Uses.
Cymogene.	0°—18°.	It is liquified by pressure and the liquid is used in refrigeration (ice making).
Rhigolene.	18°-40°.	Local anaesthetic.
Gasolene (Petroleum ether.)	40°-90°.	Solvent for fats and oils, used in dry cleaning; it forms a small part of ordinary petrol.
Ligroin (Petroleum Naphtha).	90°-120°.	Used in dry cleaning and forms the major portion of petrol.
Benzolin (Petroleum Benzine).	120°-150°	Dry cleaning.
Kerosine (Burning oil).	150°-300°	Illuminant, fuel, oil gas.
Lubricating oil.	above 300°.	Lubrication.
Petroleum jelly (Vaselines).	Semi-solid.	Toilet preparations and ointments.
Parrafin wax.	Solid.	Candle industry.

Determination of the Molecular Formula of a Gaseous Hydrocarbon.

A known volume of the gaseous hydrocarbon is exploded with excess of oxygen (known volume). The reduction in volume after explosion is noted.

The resulting mixture of gases is treated with caustic potash solution, which will absorb all the carbon dioxide. Therefore, reduction in volume after treatment with caustic potash will be the volume of carbon dioxide formed.

The volume which remains after treatment with caustic potash must be the volume of surplus oxygen. From this volume of surplus oxygen the volume of oxygen consumed can be obtained by difference.

These figures are quite sufficient for the determination of the molecular formula of the hydrocarbon. The calculations will become clear from an example.

Example :—20 *c. c.* of a gaseous hydrocarbon were mixed with 100 *c. c.* of oxygen (excess) and exploded. The volume after explosion was found to be 90 *c. c.* The volume after treatment with caustic potash was 50 *c. c.* What is the molecular formula of the hydrocarbon ?

Solution 1. Let $CxHy$ be the formula of the hydrocarbon. The equation for its combustion will be :

$$CxHy+\left(x+\frac{y}{4}\right)O_2=xCO_2+\frac{y}{2}H_2O.$$

This shows that one molecule of the hydrocarbon gives x molecules of carbon dioxide.

Or applying Avogadro's Hypothesis, one volume of the hydrocarbon gives x volumes of carbon dioxide.

20 c. c. of the hydrocarbon will give 20 x c. c. of carbon dioxide.

From the data the volume of carbon dioxide is 40 c. c. (the volume taken up by caustic potash).

$$\therefore \quad 20x = 40.$$
$$\text{or } x = 2$$

To find the value of y we take the help of the reduction in volume after explosion. The equation shows that one volume of the hydrocarbon requires $x + \frac{y}{4}$ volumes of oxygen.

20 c. c. of the hydrocarbon will require $20\left(x + \frac{y}{4}\right)$ c. c. of oxygen.

The total volume consumed

$$= 20 + 20\left(x + \frac{y}{4}\right) \text{ c.c.,}$$

while we get only 20 x. c. c. of carbon dioxide (water, being in the liquid state at ordinary temperatures, is neglected.)

The reduction in volume $= 20 + 20\left(x + \frac{y}{4}\right) - 20\,x.$

This is equal to the observed reduction, 30 c. c.

$$\therefore \quad 20 + 20\left(x + \frac{y}{4}\right) - 20\,x = 30.$$

$$\begin{aligned} \text{or} \quad 20+20x+5y-20x &= 30. \\ \text{or} \quad 5y &= 30-20=10. \\ \text{or} \quad y &= 2. \end{aligned}$$

Therefore the formula of the hydrocarbon is C_2H_2 (acetylene).

Solution 2. *Alternative method*—There is yet another method for solving this question without making use of this equation.

The volume of the carbon dioxide produced is 40 *c.c.* This must have been produced from 20 *c.c.* of the hydrocarbon, because there is no other source of this gas. 20 *c. c.* of the hydrocarbon gives 40 *c. c.* of carbon dioxide; therefore one *c.c.* will give two *c.c.* of carbon dioxide Or applying Avogadro's Hypothesis, one molecule of the hydrocarbon gives two molecules of carbon dioxide.

Two molecules of carbon dioxide contain two atoms of carbon. Therefore one molecule of the hydrocarbon contains two atoms of carbon. The only thing that remains is to find out the number of hydrogen atoms.

The volume of oxygen consumed = 100-50 = 50*c.c.*

The volume of carbon dioxide produced = 40 *c c.*

Therefore out of the total volume of oxygen consumed (50 *c.c.*), 40 c. c. has been taken up by carbon dioxide, because carbon dioxide contains its own volume of oxygen. Therefore the remaining volume of oxygen consumed has been taken up by hydrogen

in the formation of water. This comes to be 10 *c. c.* Therefore 10 c. c. of oxygen has been consumed in formation of water. But 10 *c. c.* of oxygen requires 20 *c.c.* hydrogen. Therefore 20 c.c. of the hydrocarbon contains *in combination* 20 *c c.* of hydrogen.

or 1 *c.c.* contains 1 *c.c.* of hydrogen.

or one molecule contains one molecules of hydrogen ;

But one molecule of hydrogen contains 2 atoms

Therefore one molecule of the hydrocarbon contains 2 atoms of hydrogen.

Therefore the formula of the hydrocarbon is C_2H_2.

EXERCISES ON CHAPTER V.

1. What is a hydrocarbon? How are hydrocarbons classified?

2. How is methane prepared in the laboratory? Describe its properties.

3. In what respects do methane and ethane resemble one another?

4. What are saturated and unsaturated hydrocarbons? Illustrate your answer by concrete examples?

5 Compare the properties of methane, ethylene and acetylene in a tabular form.

6. Write down equation to illustrate the action of the following substances on methane, ethylene and acetylene :—

(*a*) Sulphuric acid
(*b*) Chlorine.
(*c*) Bromine.
(*d*) Hydrogen bromide
(*e*) Hydrogen iodide
(*f*) Hydrogen.

7. How is the formula of a gaseous hydrocarbon determined?

8. Explain the meaning of the terms 'substitution' and 'inverse substitution,' giving examples.

9. Give two methods for the preparation of ethylene and contrast the general properties of ethylene with those of ethane.

10. How is acetylene prepared? Describe its properties and uses.

11. 10 *c.c.* of a gaseous hydrocarbon were exploded with 50 *c.c.* of oxygen (excess). After cooling the residual gases occupied 45 *c.c.* The volume after treatment with caustic potash was found to be 25 *c.c.* Find out the molecular formula of the hydrocarbon.

[Answer C_2H_2].

12. A gaseous hydrocarbon was exploded with oxygen and the following observations were noted :—

Volume of the hydrocarbon	=	40 *c.c.*
Volume of oxygen added	=	100 *c.c.*
Volume after explosion	=	60 *c c.*
Volume after treatment with caustic potash	=	20 *c c.*

Calculate the molecular formula of the hydrocarbon.

[Answer CH_4].

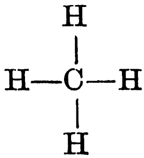
13. 20 *c.c.* of a hydrocarbon was mixed with excess of oxygen and exploded. The reduction in volume after explosion was found to be 50 *c.c.* There was a further reduction of 40 *c.c.* when the residual volume was treated with KOH. What was the molecular formula of the hydrocarbon ?

[Answer C_2H_6].

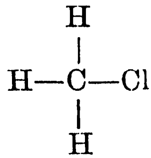
CHAPTER VI.

HALOGEN DERIVATIVES OF PARAFFINS.

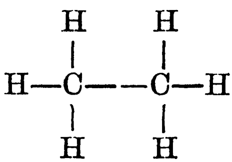
Monohalogen derivatives.—The formula of a mono-halogen derivative of a paraffin is obtained by the replacement of one atom of hydrogen in the molecule of the saturated hydrocarbon, by one atom of the halogen.



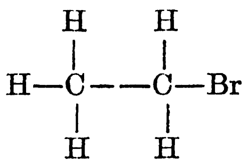
Methane.



Methyl chloride or Monochloro-methane.



Ethane.



Monobromo-ethane or Ethyl bromide.

Two methods of the formation of the mono-halogen derivatives of paraffins have already been mentioned:—

1. When methyl and ethyl alcohols are treated with phosphorus pentachloride, methyl and ethyl chlorides are respectively obtained.

$$CH_3OH + PCl_5 = CH_3Cl + HCl + POCl_3.$$

$$C_2H_5OH + PCl_5 = C_2H_5Cl + HCl + POCl_3.$$

The tri-halides of phosphorous give similar results.

$$3CH_3OH + PCl_3 = 3CH_3Cl + H_3PO_3.$$

$$3C_2H_5OH + PBr_3 = 3C_2H_5Br + H_3PO_3.$$

$$3C_2H_5OH + PI_3 = 3C_2H_5I + H_3PO_3.$$

In the case of bromine and iodine, sometimes the halogen and phosphorus are employed instead of the tri-halide.

2. When chlorine or bromine is left in contact with a saturated hydrocarbon in diffused sunlight, substitution takes place.

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$
$$C_2H_6 + Br_2 = C_2H_5Br + HBr.$$

This reaction is not applicable to the iodine derivatives, owing to the formation of hydrogen iodide which brings about inverse substitution.

Monohalogen derivatives are not the only products of such a reaction of substitution. Other hydrogen atoms also may be similarly replaced by the halogen and it is very difficult to arrest the reaction at the required stage.

The above two methods are employed only when the other more convenient methods are not available.

These derivatives are more conveniently prepared by the action of the hydracids of the halogens on the corresponding alcohol.

$$CH_3OH + HCl = CH_3Cl + H_2O.$$
$$C_2H_5OH + HBr = C_2H_5Br + H_2O.$$

This method also is not applicable to the iodine derivatives owing to the reducing action of hydrogen iodide which brings about the reverse change.

Preparation of Ethyl Chloride. **Experiment 6**. Fit up an apparatus as shown in Figure 7, A rapid current of hydrogen chloride gas is passed through a mixture of absolute alcohol and zinc chloride contained in the flask *A* which is heated on the water bath. The flask *B* contains water and the delivery tube from the flask *A* ends just above the surface of water. The tower *C* contains soda-lime. The flask *B* and the tower *C* take up the hydrogen chloride which

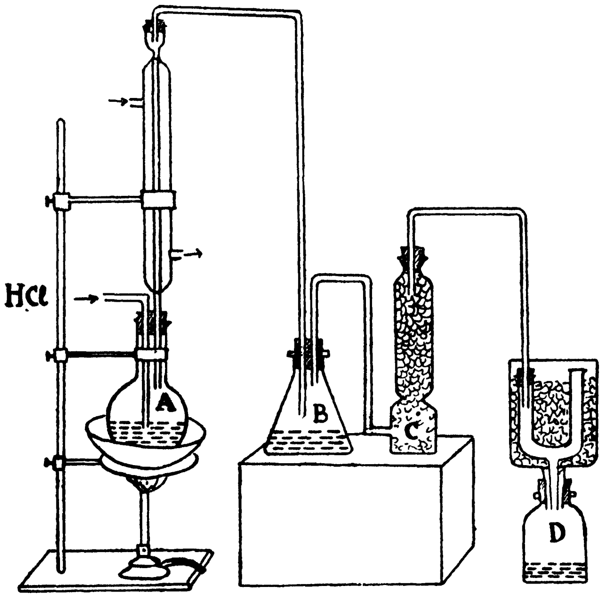


Fig. 7.

is associated with the vapours of ethyl chloride. The vapours are finally lead through a U-tube surrounded by ice. Ethyl chloride collects in the bottle *D*.

The function of anhydrous zinc chloride is to take up water which is produced by the reaction between the alcohol and hydrogen chloride.

Preparation of Ethyl Bromide **Experiment 7.** To a well cooled mixture of 15 c.c. of conc. sulphuric acid and 20 c c. of good rectified

spirit, contained in a litre flask, add about 30 grams of potassium bromide. Leave it alone for some time. Fit up the apparatus a shown in the figure and carefully distil on a sand bath. Collect the distillate under water.

Transfer the distillate to a separating funnel. Ethyl bromide being heavier, forms the lower layer. Separate this layer from the lighter aqueous layer and wash twice with a weak solution of sodium carbonate. This will remove hydrobromic acid. Now wash it twice with water and finally dry it with fused calcium chloride and distil.

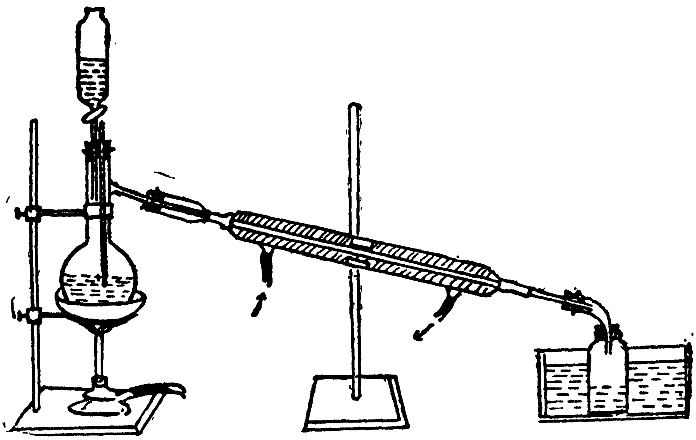


Figure 8.

Chemical properties of Monohalogen derivatives. In chemical properties also they closely resemble one another as in the case of physical properties.

1. When they are **reduced with nascent hydrogen** (*e. g.*, produced from $Zn + H_2SO_4$), they give the corresponding hydrocarbon.

$$CH_3\ \boxed{I+H}\ H = CH_4 + HI.$$

Methane.

$$C_2H_5\ \boxed{I+H}\ H = C_2H_6 + HI.$$

Ethane.

2. When **treated with metallic zinc, or sodium,** they give higher hydrocarbons.

$$CH_3\ \boxed{\begin{matrix}I+I\\+\\Zn\end{matrix}}\ CH_3 = C_2H_6 + ZnI_2.$$

Ethane

$$C_2H_5\ \boxed{\begin{matrix}I+I\\+\\Na\quad Na\end{matrix}}\ C_2H_5 = C_4H_{10} + 2NaI.$$

Butane.

3. With **aqueous caustic potash,** corresponding alcohols are obtained.

$$CH_3\ \boxed{I+K}\ OH = CH_3OH + KI.$$

Methyl alcohol.

$$C_2H_5\ \boxed{Br+K}\ OH = C_2H_5OH + KBr.$$

Ethyl alcohol.

4. With **alcoholic caustic potash,** unsaturated hydrocarbons of ethylene series are produced.

$$C_2H_5I = C_2H_4 + HI.$$

Ethylene.

5. **Potassium cyanide** (KCN) gives the corresponding cyanide,

$$CH_3\ \boxed{Cl+K}\ CN = CH_3CN + KCl.$$

Methyl cyanide.

$$C_2H_5\ \boxed{Br+K}\ CN = C_2H_5CN + KBr.$$

These cyanides are of great synthetic value.

6. **Alcoholic ammonia** (ammonia dissolved in alcohol) gives the corresponding amines. The

halogen atom is replaced by a monovalent amino group ($-NH_2$).

$$CH_3 \,|\, \overline{\underline{I + H}} \,|\, NH_2 = CH_3NH_2 + HI.$$

Methyl amine.

$$C_2H_5 \,|\, \overline{\underline{I + H}} \,|\, NH_2 = C_2H_5NH_2 + HI.$$

Ethyl amine.

Owing to their great chemical activity, the monohalogen derivatives are used as important synthetic agents.

Dihalgen Derivatives of Paraffins. The dihalogen derivatives of paraffins are substances, the formulæ of which are obtained by the replacement of two hydrogen atoms, from the molecules of the hydrocarbons by two halogen atoms.

These are not of very great importance. A few names may only be mentioned.

CH_2Cl_2 dichlro-methane or methylene chloride.

$C_2H_4Cl_2$ ethylene and ethylidene dichlorides.

$C_2H_4Br_2$ ethylene and ethylidene dibromides.

Trihalogen Derivatives of Paraffins. Two members of this group are of great medical importance. Chloroform, ($CHCl_3$) is the well known anaesthetic while iodoform (CHI_3) has been used in surgery as a very valuable antiseptic and disinfectant.

CHLOROFORM. $CHCl_3$.

Chloroform is tri-chloro-methane *i. e.*, methane in which three out of the four atoms of hydrogen in each molecule have been replaced by chlorine.

$$\begin{array}{c} Cl \\ | \\ H-C-Cl \\ | \\ Cl \end{array}$$

Preparation. 1. In small quantities it is formed when methane is directly *chlorinated* in the presence of sunlight.

$$CH_4 + 3Cl_2 = CHCl_3 + 3HCl.$$

This method is only of theoretical importance.

2. Pure chloroform may be obtained by distilling chloral or chloral hydrate with caustic soda.

Experiment 8. Take a little chloral hydrate in a test tube and add caustic soda solution and shake gently. The characteristic sweet smell of chloroform is observed.

3. Chloroform is usually prepared in the laboratory (and also manufactured) by the distillation of a mixture of bleaching powder and alcohol or acetone.

Experiment 9. A paste of bleaching powder and water [200 grams of good bleaching powder and 800 grams of water] is taken in a large round bottom flask. To this is added 500 c,c. of ethyl alcohol or acetone. The flask is then fitted with a condenser and the contents are cautiously distilled on a sand bath. The distillation is continued till the oily drops cease to come over. It is purified in the same way as ethyl bromide.

A better method is to chlorinate alcohol or acetone and then to distil with slaked lime and a little bleaching powder.

[For chemical changes in (2) and (3) see chloral].

Properties. Chloroform is a colourless heavy liquid (sp. gr. 1·528). It boils at 61°C. and possesses a characteristic sweet odour. It is non-inflammable under ordinary conditions. It is not miscible with water.

If it is boiled with caustic potash it decomposes giving potassium formate and potassium chloride.

$$CHCl_3 + 4KOH = HCOOK + 3KCl + 2H_2O.$$

Pure chloroform gives no precipitate with silver nitrate (distinction from metallic chlorides).

If exposed to sunlight in contact with air, it decomposes forming free chlorine and carbonyl chloride ($COCl_2$).

$$2CHCl_3 + 3O = 2COCl_2 + Cl_2 + H_2O.$$

Uses. Chloroform is a valuable anaesthetic. Its anaesthetic action was first pointed out by Sir J. Y. Simpson of Edinburgh in 1848, and it was ultimately introduced in surgery. It has replaced practically all the anaesthetics previously used in surgery ; but owing to its unpleasant after-effects, new anaesthetics *e. g.*, ethylene and specially local anaesthetics are being introduced.

It has been mentioned that if chloroform is exposed to light in contact with air, it decomposes to give carbonyl chloride and free chlorine. Both these substances are poisonous. Therefore chloro-

form which is used as an anaesthetic must be free from these impurities. To avoid the formation of these impurities chloroform is preserved in the dark, in small bottles which are kept filled up to the neck.

It is also used as a solvent for sulphur, phosphorus, iodine, oils, fats, resins and many other organic compounds, which are not soluble in water.

To Distinguish Pure Chloroform from Decomposed Chloroform—Pure chloroform does not give a precipitate with silver nitrate solution, but if it contains carbonyl chloride, the usual white precipitate of silver chloride is thrown down on the addition of silver nitrate.

The carbonyl chloride is hydrolysed by water forming hydrochloric acid which gives a precipitate with silver nitrate.

$$COCl_2 + H_2O = 2HCl + CO_2.$$

$$HCl + AgNO_3 = AgCl + HNO_3.$$

Distinguishing tests.

1. Sweet smell.
2. With water it forms a lower layer.
3. Gives a characteristic bad smell when warmed with aniline and caustic potash or caustic soda.

Experiment 10. Take a few c. c. of caustic soda or caustic potash in a test-tube and add a few drops of aniline followed by a drop or

two of chloroform and warm. A characteristic offensive smell is observed.

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5NC + 3KCl + 3H_2O$$

IODOFORM. CHI_3.

Iodoform is tri-iodo-methane. It is not formed by direct substitution.

Preparation. It is prepared by warming together the required quantities of alcohol or acetone, iodine, and an alkali.

Experiment 11. *(a)* Take a small quantity of alcohol or acetone in a test-tube. Add iodine solution (iodine dissolved in potassium iodide). Now add dilute caustic soda drop by drop till the colour of iodine is discharged. Add iodine solution again. Yellow crystals of iodoform possessing characteristic smell will be formed.

(b) Take about 50 c.c. of water in a beaker. Add to it 10 grams of sodium carbonate and 5 grams of iodine and a little alcohol. Warm in a water bath. Yellow crystals of iodoform will separate out. Filter and wash with water.

Iodoform is now manufactured by the electrolysis of a solution of potassium iodide in the presence of alcohol or acetone and a little sodium carbonate. A similar method is applied to the preparation of chloroform.

Properties. Iodoform is a lemon yellow, solid, crystalline substance having a characteristic odour. It melts at 119°C. It is insoluble in water but dissolves to some extent in alcohol, and ethyl acetate.

When iodoform is boiled with caustic potash it decomposes :

$$CHI_3 + 4KOH = \underset{\text{Potassium formate.}}{HCOOK} + 2H_2O + 3KI.$$

Therefore when caustic alkalies are used in its preparation, the mixture should not be boiled.

Uses. Iodoform was very extensively used as an antiseptic and disinfectant in surgery but owing to its high price and bad smell it is being replaced by other cheaper and odourless substances.

Tetra-halogen Derivatives of Paraffins.

Carbon Tetrachloride. CCl_4. Carbon tetrachloride or tetra-chloro-methane is prepared by the action of chlorine on carbon disulphide, in the presence of iodine which works as a chlorine carrier.

$$3CS_2 + 6Cl_2 = 3CCl_4 + 6S.$$

Properties. Carbon tetrachloride is a colourless, sweet smelling liquid which boils at 76°C. It is non-inflammable and is therefore used in fire extinguishers. It is also used as a solvent for fats or oils. In small doses it is given to patients suffering from hook-worms of the intestines.

EXERCISES ON CHAPTER VI.

1. What do you understand by the expression "Monohalogen Derivatives of Paraffins',? Write down the names and formulae of some of these derivatives.

2. Describe with full practical details the preparation of Ethyl Bromide. How is ethyl bromide purifide?

3. How does ethyl bromide behave towards the following substances: Nascent hydrogen, potassium cyanide, alcoholic caustic potash, aqueous potash, metallic zinc, and sodium?

Give equations for all the reactions.

4. How is chloroform prepared and purified? Describe its properties.

5. Describe the preparation and properties of iodoform.

6. What is the action of boiling caustic soda or caustic potash on iodoform and chloroform?

7. What substances are produced when chloroform is exposed to sunlight? How can pure chloroform be distinguished from such decomposed chloroform? What is the importance of such a distinction?

8. How would you prepare chloroform in the laboratory? How would you show the presence of chlorine in chloroform?

a small quantity of pure chloroform is exposed to sunlight in a large colourless glass bottle, would the chloroform still remain pure, if not, how would you prove it.

9. What is iodoform? How is it manufactured and how is it prepared in the laboratory? Describe its properties. What is the action of boiling caustic potash on iodoform?

10. Describe with experimental details, how chloroform is prepared. Draw a sketch of the apparatus used. What are its more important properties?

CHAPTER VII.

ALCOHOLS.

Reference has already been made to methyl and ethyl alcohols with regard to their manufacture, purification and some of their properties. It has been shown there that they closely resemble one another in their properties.

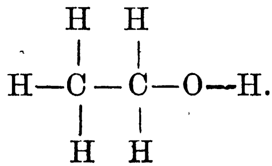
These are only the first and second members of a homologous series called *alcohols.* They very well represent the properties of their class.

The formula of an alcohol is obtained by the replacement of an atom of hydrogen in the molecule of a hydrocarbon by a **Hydroxyl group** (—OH). When we compare the formula of ethyl alcohol (C_2H_6O) with that of the corresponding hydrocarbon (ethane, C_2H_6), we observe that one atom of oxygen has entered the molecule of ethane. But if we believe the constitutional formula of ethane to be,

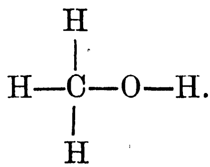
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

there is no place in the molecule of ethane for an atom of oxygen, because valencies of all the carbon

atoms are fully satisfied. There are reasons to believe that the arrangement of atoms in the molecule of ethyl alcohol is,



and that of methyl alcohol is



(See Constitution of Ethyl Alcohol at the end of this Chapter).

There must be something common in their constitution which may be regarded as the cause of their similar properties. On examining the constitutional formulae of these two alcohols and also of other alcohols, it will be observed that they contain the monovalent —OH group, the other valencies of the carbon atom or atoms being satisfied by hydrogen atoms.

Therefore the monovalent hydroxyl group is the characteristic group of all the alcohols. The remaining portion of the molecule is called the **Alkyl Group** and is generally represented by the letter R, so that the general formula of an alcohol is R — O — H

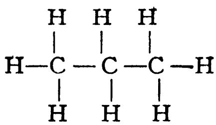
where R may be a methyl, an ethyl or a propyl group etc.

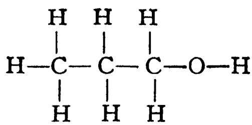
$-CH_3$	$-C_2H_5$	$-C_3H_7$	$-C_4H_9$
Methyl group	Ethyl group	Propyl group	Butyl group

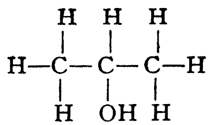
If propane is taken and somehow, one of the 8 hydrogen atoms is replaced by a hydroxyl group, two different alcohols will be obtained with the same molecular formula :—

(1) in which the hydroxyl group is attached to one of the end carbon atoms ;

(2) in which the hydroxyl group is attached to the middle carbon atom,


Propane


(1)


(2)

Actually two such substances are known. They have different properties *i. e.*, they are quite different chemical substances.

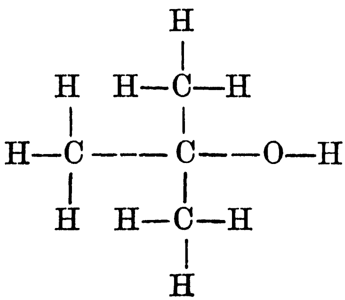
This shows that the properties of a substance do not depend only on the nature of the elements present and on the number of the atoms of each element but also on the arrangement of the atoms in the molecule. Substances can exist which have the same molecular formula but absolutely different properties.

The occurrence of more than one substance with the same molecular formula is know as **isomerism** and the substances are known as **isomers.**

An alcohol in which the hydroxyl group is attached to an end carbon atom, is called a **Primary Alcohol.** In the case of propyl alcohol the alcohol No. (1) is the primary alcohol. Methyl and ethyl alcohols also are primary alcohols.

An alcohol in which the hydroxyl group is attached to a middle carbon which is attached to two other carbon atoms, is known as a **Secondary Alcohol.** No. (2) is the Secondary Propyl Alcohol.

There may be a third case where the hydroxyl group is attached to a middle carbon atom, which itself is attached to three other carbon atoms. Such an alcohol is called a **Tertiary Alcohol.**



Tertiary butyl alcohol.

Comparing the formulae of the primary, secondary, and tertiary alcohols, it will be observed that they have the following characteristic groups :—

Primary	$-CH_2-OH$	The free valency is satisfied with hydrogen or carbon.
Secondary	$=CH-OH$	The free valencies are satisfied by carbon.
Tertiary	$\equiv C-OH$	The free valencies are satisfied by carbon.

Properties of Ethyl Alcohol. It has already been mentioned that in its behaviour towards acids, ethyl alcohol resembles caustic soda.

$$Na\,\boxed{OH + H}\,Cl = NaCl + H_2O.$$
$$C_2H_5\boxed{OH + H}\,Cl = C_2H_5Cl + H_2O.$$
$$Na\boxed{OH + H}\,HSO_4 = NaHSO_4 + H_2O.$$
$$C_2H_5\boxed{OH + H}\,HSO_4 = C_2H_5HSO_4 + H_2O.$$

while in its behaviour towards sodium and phosphorus pentachloride it resembles water.

$$2H_2O + 2Na = 2NaOH + H_2.$$
$$2C_2H_6O + 2Na = 2C_2H_5ONa + H_2.$$
$$H_2O + PCl_5 = HCl + POCl_3 + HCl.$$
$$C_2H_6O + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

Action of Sulphuric Acid. Ethyl alcohol behaves in four different ways towards sulphuric acid, according to the conditions of the experiment.

1. **At 0° C. using fuming sulphuric acid,** diethyl sulphate is produced.

$$2C_2H_5OH + H_2SO_4 = (C_2H_5)_2SO_4 + 2H_2O.$$

2. **At 100°C, using equal volumes** of concentrated sulphuric acid and alcohol ethyl hydrogen sulphate is produced.

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

3. **At 140°C, with excess of alcohol** the product is diethyl ether (see ether).

$$2C_2H_5OH = C_2H_5-O-C_2H_5 + H_2O.$$

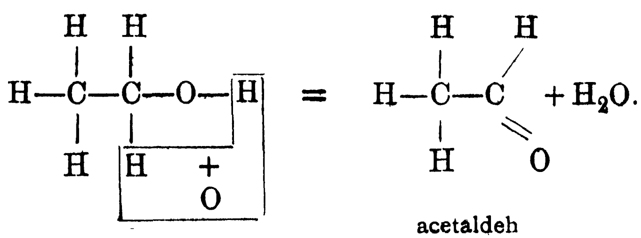
4. **At 165°C, with excess of sulphuric acid,** ethylene is produced.

$$C_2H_5OH = C_2H_4 + H_2O.$$

This is a very good example to illustrate that the same substance may be made to react in different ways by changing the conditions—a state of affairs rarely to be found in the study of inorganic reactions.

Oxidation of Ethyl Alcohol. By regulated oxidation, ethyl alcohol gives different products.

1. The first step in the oxidation of ethyl alcohol is the formation of acetaldehyde. The molecule of alcohol loses two atoms of hydrogen, (one from the hydroxyl group and the other from that carbon atom to which the hydroxyl group is attached).



acetaldeh

This oxidation may be brought about by using potassium dichromate and sulphuric acid or potassium permanganate and sulphuric acid as oxidising agents.

2. The second stage is the oxidation of acetaldehyde to acetic acid.

$$CH_3CHO + O = CH_3COOH.$$

Ethyl alcohol may directly be oxidised to acetic acid.

$$C_2H_5OH + 2O = CH_3COOH + H_2O.$$

3. The third stage is the combustion of ethyl alcohol to carbon dioxide and water.

$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O.$$

Action of Chlorine on Ethyl Alcohol. Chlorine first oxidises ethyl alcohol to acetaldehyde, and then works as a substituent forming chloral.

$$C_2H_5OH + Cl_2 = CH_3CHO + 2HCl.$$
$$CH_3CHO + 3Cl_2 = \underset{\textbf{Chloral.}}{CCl_3CHO} + 3HCl.$$

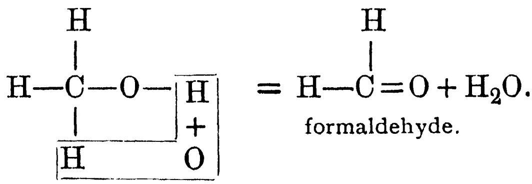
Uses of Ethyl Alcohol. It is used as a solvent in various manufacturing processes *e. g.*, in the preparation of varnishes, paints, dyes and prefumes etc. It is also used in the manufacture of acetic acid, ether, chloroform and iodoform. All spirits and tinctures of the druggist contain ethyl alcohol. In biological laboratories it is used as a preservative of biological specimens. In chemical laboratories it is a very useful solvent. Many substances which do

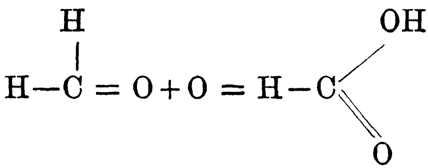
not dissolve in water are soluble in alcohol, *e. g.*, benzoic acid, camphor, sulphur.

Methylated spirit mainly consists of ethyl alcohol, and is extensively used as a fuel and solvent.

Ethyl alcohol is the active constituent of all alcoholic drinks.

Properties of Methyl Alcohol. Some of the properties of methyl alcohol have already been described. In its behaviour towards oxidising agents methyl alcohol exactly resembles ethyl alcohol.

1. 

2. 

formic acid.

3. $2CH_3OH + 3O_2 = 2CO_2 + 4H_2O$.

Methyl alcohol does not give iodoform when it is treated with iodine and an alkali.

When methyl alcohol is warmed with salicylic acid and conc. sulphuric acid, the smell of the oil of winter green is observed, owing to the formation of methyl salicylate.

Uses of Methyl Alcohol. It is used in the preparation of methylated spirit, and also as a solvent in

the preparation of certain varnishes, lacquers, dyes, drugs and perfumes etc. Formalin is prepared by the oxidation of methyl alcohol.

To Distinguish Between Methyl Alcohol and Ethyl Alcohol. Physical properties are the chief criteria of purity of organic compounds. Therefore the two alcohols may be distinguished from each other by the help of their boiling points, provided the substances are pure. If impurities are present the presence of the two alcohols may be detected by the following tests :—

1. Treat the substance with iodine and caustic soda, if iodoform is produced, it indicates the presence of ethyl alcohol (see iodoform).

2. Heat the substance with salicylic acid and conc. sulphuric acid. If methyl alcohol is present, smell of oil of winter green will be observed.

Constitution of Ethyl Alcohol. It has been shown in the beginning of this chapter that two substances may occur having the same molecular formula, and that this can only be due to the different arrangement of atoms in the molecules of the two substances. Therefore after the determination of the molecular formula of a substance, it is necessary to try to find out the arrangement of atoms in the molecule of the substance. A formula which shows the probable arrangement of atoms in the molecule is known as the **constitutional formula** of the substance.

It has been mentioned that the molecular formula of ethyl alcohol is C_2H_6O. When ethyl alcohol is treated with sodium, hydrogen is evolved and also a solid substance is produced with the molecular formula C_2H_5ONa (sodium ethylate). Whatever be the relative quantity of sodium used, the ultimate products are the same (hydrogen and sodium ethylate). This shows that out of the six atoms of hydrogen contained in the molecule of ethyl alcohol, it is only one which can be replaced by sodium. If all the six atoms of hydrogen were similarly situated in the molecule, all the six should have been replaceable by sodium. But the molecule contains only one hydrogen atom which can be replaced by metal. Therefore this atom of hydrogen has got a position in the molecule which is quite different from those of the remaining five atoms of hydrogen. This atom of hydrogen may be represented separately in the formula as $C_2H_5O—H$.

When ethyl alcohol is treated with phosphorus pentachloride, a reaction takes place according to the following equation :—

$$C_2H_6O + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

This shows that in the formation of ethyl chloride (C_2H_5Cl), the atom of chlorine has taken the place of an atom of oxygen and an atom of hydrogen. Had the atom of oxygen and the atom of hydrogen, which have gone out, been *separately* attached to the remaining portion of the molecule, they should

have vacated three valencies. But their place has been taken by only one atom of chlorine, which is monovalent. Therefore it is highly probable that the atom of oxygen and the atom of hydrogen are attached to the remaining portion of the molecule only by single valency. According to this assumption, the formula of ethyl alcohol may be written as $C_2H_5.OH$.

There remains only to show the relative positions of the two carbon atoms and the five hydrogen atoms and also to find out which of the hydrogen atoms is replaceable by sodium.

When ethane is treated with chlorine, ethyl chloride is obtained. If the constitution of ethane is

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

that of ethyl chloride should be

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & Cl. \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

When ethyl chloride is treated with aqueous caustic potash, ethyl alcohol is the product. The molecule of ethyl chloride loses an atom of chlorine but gains an atom of oxygen and an atom of hydrogen. It appears to be highly probable that these atoms of hydrogen and oxygen together take the place of the

out going atom of chlorine, creating the hydroxyl group in the molecule, which is further supported by the arguments based on the action of phosphorus pentachloride.

Considering all the above arguments, it appears that the constitutional formula of ethyl alcohol is

$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H. \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

It is the atom of hydrogen of the hydroxyl group *i. e.*, the atom of hydrogen which in the above formula is directly attached to the oxygen atom which has got a unique position in the molecule. The remaining five atoms of hydrogen are directly attached to one or the other carbon atom. Therefore it is the hydrogen atom of the hydroxyl group which is replaceable by sodium.

EXERCISES ON CHAPTER VII.

1. What are primary, secondary and tertiary alcohols?

2. How does sulphuric acid behave towards ethyl alcohol?

3. What are the oxidation products of ethyl alcohol?

4. You are supplied with dilute aqueous solutions of ethyl alcohol and methyl alcohol, How will you distinguish between the two?

5. What is "Isomerism"?

6. What is the action of chlorine on ethyl alcohol?

7. How is the constitutional formula of ethyl alcohol established?

8. What are the uses of ethyl and methyl alcohols?

9. Write down the formulæ of the primary, secondary and tertiary alcoholic groups.

10. Write down equations to illustrate the action of the following substances on ethyl alcohol:—

Sodium, phosphorus chlorides, chlorine, potassium dichromate and sulphuric acid, iodine and sodium carbonate, and hydrochloric acid.

11. When the juice of the grape is exposed to the air, alcohol is produced. Explain as fully as you can, what takes place.

CHAPTER VIII.

ETHERS

Ethers may be regarded as the alkyl oxides. They are related to the alcohols in the same way as sodium oxide is related to sodium hydroxide.

$$\begin{matrix} Na \diagdown & \\ & O \\ Na \diagup & \end{matrix} \qquad\qquad \begin{matrix} C_2H_5 \diagdown & \\ & O \\ C_2H_5 \diagup & \end{matrix}$$

$$Na—O—H \qquad\qquad C_2H_5—O—H$$

The analogy should not be carried beyond their constitution. The general formula of ethers is the same as that of alcohols, but unlike alcohols, they do not contain any hydroxyl group. They contain two alkyl groups joined together through oxygen.

$C_2H_5—O—C_2H_5$ Di-ethyl ether.

$CH_3—O—CH_3$ Di-methyl ether.

DI-ETHYL ETHER, $C_2H_5—O—C_2H_5$.

Di-ethyl ether which is also known as common ether or simply ether is the most important member of the class.

Preparation 1. In the laboratory and also on the large scale, ether is prepared by heating ethyl alcohol with concentrated sulphuric acid at about 145°C. using excess of alcohol.

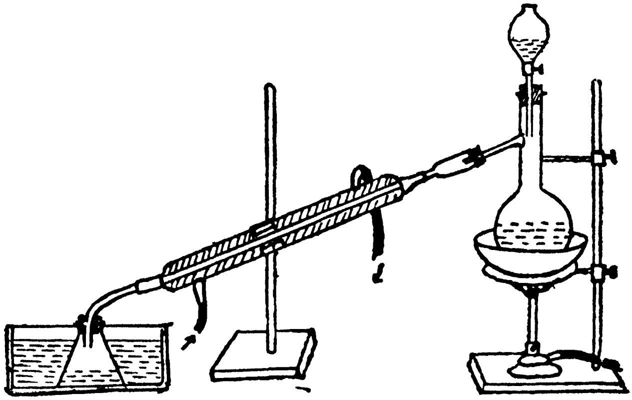


Fig. 9.

Experiment 12. Fit up an apparatus as shown in the figure. In the distilling flask take five parts of conc. sulphuric acid and nine parts of absolute alcohol or good rectified spirit. The bulb of the thermometer should dip in the liquid of the flask. Put some alcohol in the dropping funnel. Heat on a sand bath and keep the temperature at about 145°C. The receiver should be cooled in ice-cold water.

Alcohol should be added from the dropping funnel almost at the same speed at which the distillation is proceeding.

The distillate contains alcohol, water, and some sulphur dioxide as impurities. It is shaken with dilute sodium carbonate solution and then with water in a tap funnel. Ether being lighter and immiscible, will form the upper layer. It is dried with fused calcium chloride and finally distilled from a water bath.

The quantity of sulphuric acid which is once taken in the flask, is capable of converting a large amount of alcohol into ether. For this reason the process is known as "**the continuous etherification process..**"

Comparing the formula of ether with that of ethyl alcohol, the change appears to be as represented by the equation

$$2C_2H_5OH = C_2H_5-O-C_2H_5+H_2O.$$

It appears that sulphuric acid acts as a dehydrating agent. But the fact that both ether and water are received in the distillate, makes it highly improbable that the acid will take away water from ethyl alcohol and will also part with it at the same temperature. It is believed and also supported by facts that alcohol forms ethyl hydrogen sulphate with sulphuric acid which reacts with more of alcohol to produce ether and regenerates sulphuric acid.

1. $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$
2. $C_2H_5HSO_4 + C_2H_5OH = C_2H_5-O-C_2H_5 + H_2SO_4.$

Adding we get: $2C_2H_5OH = C_2H_5-O-C_2H_5+H_2O.$

Water and ether distil over and sulphuric acid reacts with fresh quantities of alcohol. The cycle goes on and the acid can convert (theoretically) an indefinite quantity of alcohol into ether. But in practice a part of sulphuric acid is reduced to sulphur dioxide and this loss has to be made good from time to time.

2. Ether may also be prepared by the action of ethyl iodide on sodium alcoholate.

$$C_2H_5\boxed{I + Na}-O-C_2H_5 = C_2H_5-O-C_2H_5+NaI.$$

Properties. Diethyl ether is a thin mobile liquid, very volatile, and highly inflammable. It boils at 35°C. It possesses a fragrant characteristic odour. It is lighter than water in which it is only very sparingly soluble. It is miscible with alcohol and is itself a very useful solvent for many substances like resins, fats, oils and alkaloids and also phosphorus, sulphur and iodine.

When inhaled it causes unconsciousness, and was formerly used as an anaesthetic. Owing to its rapid evaporation, it was used as a local anaesthetic in minor surgical operations. It is unaffected by ammonia, dilute acids or metallic sodium. Under ordinary conditions phosphorus halides have no action on ether, but when the mixture is heated, the oxygen atom of the ether molecule is replaced by two halogen atoms, giving ethyl halide:

$$C_2H_5—O—C_2H_5 + PCl_5 = 2C_2H_5Cl + POCl_3.$$

No hydrochloric acid is evolved in the reaction (distinction from alcohol).

Saturated with hydrogen iodide at 0°C it gives alcohol and ethyl iodide.

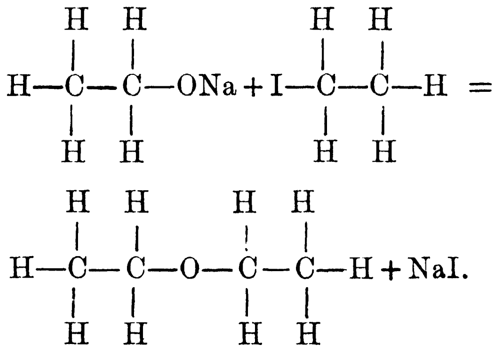
$$C_2H_5—O—C_2H_5 + HI = C_2H_5OH + C_2H_5I.$$

Towards ether, halogens work as substituents and not as oxidising agents (see alcohol).

Uses. Ether is used for the extraction of fats and oils. It is a very good solvent for resins, alkaloids, sulphur, and iodine. It is also used in refrigerating machines.

Constitution of Diethyl Ether.

The molecular formula of common ether is $C_4H_{10}O$. The formation of the substance from ethyl iodide and sodium ethoxide clearly shows that the two ethyl groups are linked through oxygen.



Moreover the action of PCl_5 on ether shows that it does not contain any hydroxyl group which is evidently in accordance with the above constitution.

Other ethers may similarly be prepared and possess similar properties. They are named after the alkyl groups which are contained in the molecule.

$CH_3—O—CH_3$ dimethyl ether.

$CH_3—O—C_2H_5$ methyl ethyl ether.

When the two alkyl groups contained in a molecule of ether are the same, the ether is called as a **simple ether**, while when they are different, it is known as **mixed ether**. Dimethyl ether and diethyl ether are examples of simple ethers while methyl ethyl ether is a mixed ether.

Methyl propyl ether (CH_3—O—C_3H_7) is isomeric with diethyl ether (C_2H_5—O—C_2H_5). Such an isomerism where the isomers belong to the same class and the isomerism is due to the presence of different alkyl groups, is known as **Metamerism.**

EXERCISES ON CHAPTER VIII.

1 Write down the full constitutional formulæ of diethyl ether, dimethyl ether, and methyl ethyl ether.

2. How is common ether prepared in the laboratory? Give practical details of the experiment.

3. What are the different methods by which an ether may be obtained?

4. What is the "continuous etherification process?" How do you account for it?

5. What are the properties of common ether?

6. How does sulphuric acid behave towards ethyl alcohol? Describe briefly the conditions under which the various products are formed.

7. How will you distinguish between an ester and an ether?

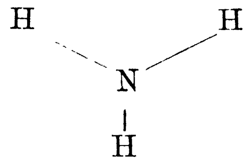
8. Write a short note on the constitution of ether.

9. Describe with all essential practical details and with the sketch of the apparatus you would use in the preparation of diethyl ether. How would you purify it and make it anhydrous. Give its structural formulae.

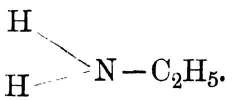
CHAPTER IX.

AMINES.

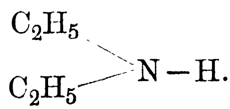
Amines are compounds which are obtained by the substitution of one, two, or all the three atoms of hydrogen in the molecule of ammonia by an equal number of alkyl radicals.



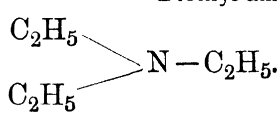
Ammonia.



Ethyl amine.



Diethyl amine.



Triethyl amine.

The amines are called Primary, Secondary, or Tertiary according as one, two or three atoms of hydrogen from the molecule of ammonia are replaced by alkyl groups. Ethyl amine ($C_2H_5NH_2$) is an example of primary amines.

Methods of Preparation of Primary Amines.

1. It was mentioned in connection with the properties of the monohalogen derivatives of paraffins

that when a monohalogen derivative of a paraffin treated with alcoholic ammonia, an amine is produced.

$$CH_3\boxed{Cl + H}-NH_2 = CH_3 \cdot NH_2 + HCl$$

But the reaction cannot be stopped at this stage. The primary amine produced as in the above equation, may react with further quantity of the alkyl halide to form other compounds.

$$CH_3NH_2 + CH_3Cl = \underset{\text{Dimethyl amine}}{(CH_3)_2NH} + HCl.$$

$$(CH_3)_2NH + CH_3Cl = \underset{\text{Trimethyl amine}}{(CH_3)_3N} + HCl.$$

$$(CH_3)_3N + CH_3Cl = \underset{\text{Tetramethyl ammonium chloride}}{(CH_3)_4NCl}.$$

By the interaction of an alkyl halide and ammonia, a mixture of all the four compounds is obtained ; and it is a difficult problem to separate these four compounds from each other. Some special methods are employed to prepare the primary amines free from the other compounds.

2. On reduction alkyl cyanides give primary amines. Hydrogen cyanide gives methyl amine.

$$HCN + 4H = CH_3NH_2 \text{ Methyl amine.}$$

$$CH_3CN + 4H = C_2H_5NH_2 \text{ Ethyl amine.}$$

3. Primary amines may also be obtained by the **Hoffmann's Reaction.** When an amide (see amides) is treated with bromine and caustic potash, a pri-

mary amine is produced, which contains one carbon atom less than the amide.

$$CH_3CONH_2 + Br_2 = CH_3CONHBr + HBr.$$

$$CH_3CONHBr + KOH = CH_3NH_2 + KBr + CO_2.$$

Hydrogen bromide and carbon dioxide produced as above will also react with caustic potash to form potassium bromide and potassium carbonate.

$$HBr + KOH = KBr + H_2O.$$

$$CO_2 + 2KOH = K_2CO_3 + H_2O.$$

The final change may, therefore, be represented by the equation,

$$CH_3CONH_2 + Br_2 + 4KOH = CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Methyl amine and Ethyl amine. Methyl and ethyl amines are homologous substances and can be prepared by any of the above methods. Both the amines are gases and possess strong ammoniacal odour. They are very soluble in water to which they impart strong alkaline properties. In many of their chemical properties they closely resemble ammonia.

Like ammonia they directly combine with acids to form salts.

$$NH_3 + HCl = NH_3HCl = NH_4Cl.$$

$$CH_3NH_2 + HCl = CH_3NH_2HCl.$$

Methyl amine hydrochloride.

$$C_2H_5NH_2 + HCl = C_2H_5NH_2HCl.$$

Ethyl amine hydrochloride.

They are not hydrolysed by any hydrolysing

agents (distinction from amides). Heated with chloroform and caustic potash, a very offensive odour of isocyanides is observed.

$$C_2H_5NH_2 + CHCl_3 + 3KOH = C_2H_5 \cdot NC + 3KCl + 3H_2O.$$

They are more strongly basic than ammonia. Their solutions freely absorb carbon dioxide from the atmosphere.

With nitrous acid, both the amines form the corresponding alcohols.

$$CH_3NH_2 + HNO_2 = CH_3OH + N_2 + H_2O.$$
$$C_2H_5NH_2 + HNO_2 = C_2H_5OH + N_2 + H_2O.$$

This reaction is anologous to the action of ammonia on nitrous acid.

$$\begin{array}{r|c|l} H- & N & =H_2 \\ \cdots\cdots\cdots & + & \cdots\cdots = H_2O + N_2 + H_2O. \\ HO- & N & =O \end{array}$$

$$\begin{array}{r|c|l} CH_3- & N & =H_2 \\ \cdots\cdots\cdots & + & \cdots\cdots = CH_3OH + N_2 + H_2O. \\ HO- & N & =O \end{array}$$

Descending a Series. The Hoffmann's Reaction may be used for the preparation of a compound containing one carbon atom less than the original compound. Supposing that we want **to prepare methyl alcohol from ethyl alcohol,** it may be accomplished by the following changes.—

$$*C_2H_5OH \xrightarrow{O} CH_3CHO \xrightarrow{O} CH_3{\cdot}COOH \xrightarrow{NH_3}$$
$$CH_3COONH_4 \xrightarrow{heat} CH_3CONH_2 \xrightarrow{Br+KOH} CH_3NH_2$$
$$\xrightarrow{HNO_2} CH_3OH.$$

Ascending a series. The reverse change *i. e.*, the **preparation of ethyl alcohol from methyl alcohol** may be brought about by any of the following two series of changes :—

1. $$*CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{Zn} CH_3CH_3 \xrightarrow{Cl}$$
$$CH_3CH_2Cl \xrightarrow{KOH} C_2H_5OH$$

2. $$*CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{H}$$
$$CH_3CH_2NH_2 \xrightarrow{HNO_2} C_2H_5OH$$

* All these reactions have been considered in the previous chapters. The students are advised to write down the equations for all the reactions.

A Comparison of Properties of Ammonia and Amines.

Properties.	Ammonia.	Methyl amine	Ethyl amine.
State.	Gas.	Gas.	Gas.
Smell	Ammonical	Ammonical	Ammonical.
Solubility in water.	Highly soluble.	Highly soluble.	Highly soluble.
Reaction in aqueous soln.	Alkaline.	Strongly Alkaline.	Strongly alkaline.
Action of HCl	Combines to form NH_4Cl	Combines to form a hydrochloride $CH_3NH_2{\cdot}HCl$.	Combines to form a hydrochloride $C_2H_5NH_2{\cdot}HCl$.
Nitrous acid.	Nitrogen evolved and HOH produced.	Nitrogen evolved and CH_3OH produced.	Nitrogen evolved and C_2H_5OH produced.

EXERCISES ON CHAPTER IX.

1. What are amines? Write down the full constitutional formulæ of ethyl amine, dimethyl amine, and trimethyl amine.

2. How does ethyl amine behave towards the following substances —

Water, caustic soda, hydrochloric acid, nitrous acid, and chloroform and caustic potash?

3. How will you prepare ethyl alcohol from methyl alcohol? Give equations for all the reactions.

4. How will you prepare methyl alcohol from ethyl alcohol? Give equations for all the reactions.

5. Starting from the elements how will you prepare samples of propionic acid and formic acid?

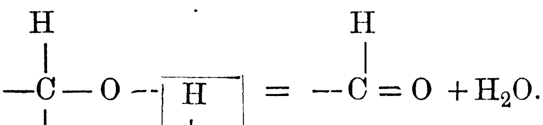
6. Compare ethyl amine with ammonia.

7. How will you obtain *(a)* acetamide from acetic acid, *(b)* methyl amine from acetamide and methyl alcohol from methyl amine? Give equations.

CHAPTER X.

FORMALDEHYDE, ACETALDEHYDE AND ACETONE.

In connection with the regulated oxidation of ethyl alcohol, it was mentioned that when ethyl alcohol is oxidised, it gives acetaldehyde and that methyl alcohol on oxidation gives formaldehyde. Both these alcohols are primary alcohols. Other primary alcohols also give similar substances (aldehydes) on oxidation. The common group in the primary alcohols is the monovalent—$CH_2.OH$ group. It is this group which on oxidation, loses two atoms of hydrogen and is converted into the aldehyde group.



aldehyde group

In the case of formaldehyde the free valency is satisfied by hydrogen, while in other cases by an alkyl group.

$$\begin{array}{c} H \\ | \\ H-C=O \end{array}$$

Formaldehyde (aldehyde of formic acid).

$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O$$ Acetaldehyde (aldehyde of acetic acid).

$$C_2H_5-\overset{\overset{\displaystyle H}{|}}{C}=O$$ Propionaldehyde (aldehyde of propionic acid).

The aldehydes are named after the acids to which they give rise on oxidation.

FORMALDEHYDE. H.CHO.

Formaldehyde is the first member of the homologous series. It contains only one carbon atom.

Preparation. 1. It is manufactured by the oxidation of methyl alcohol.

$$CH_3OH + O = H.CHO + H_2O$$

Experiment 13. Take two or three c.c. of methyl alcohol in a test tube. Heat a roll of copper gauze very strongly in a flame and introduce the hot roll in the test tube containing methyl alcohol. A strong smell of formaldehyde is observed.

When metallic copper is heated in air it is coated with a film of copper oxide which under the conditions of the experiment oxidises methyl alcohol to formaldehyde and is itself reduced to metallic copper.

2. Formaldehyde may also be obtained by heating dry calcium or barium formate.

$$\left.\begin{matrix} H.COO \\ H.COO \end{matrix}\right\rangle Ca = CaCO_3 + H.CHO.$$

$$\begin{matrix} H.CO.O \\ H.CO.O \end{matrix}\!\!>\!Ba = BaCO_3 + H.CHO.$$

Properties. Formaldehyde is a gas at ordinary temperatures. It can be condensed to a liquid which boils at $-21°C$. It possesses a characteristic pungent and very disagreeable odour. It is freely soluble in water and also in alcohol.

Gaseous formaldehyde, or its aqueous solution in the absence of methyl alcohol, quickly deposits a white substance called trioxy-methylene.

Formaldehyde can easily be oxidised and therefore it works as a strong reducing agent.

$$H.CHO + O = H.COOH \quad \text{Formic acid}.$$

Formaldehyde gives a mirror of metallic silver with an ammoniacal solution of silver nitrate. When ammonia is added drop by drop to a solution of silver nitrate, a black precipitate of hydrated silver oxide is first obtained.

$$AgNO_3 + NH_4OH = AgOH + NH_4NO_3.$$

$$2AgOH = Ag_2O + H_2O.$$

This precipitate dissolves in excess of ammonium hydroxide. When a solution of silver oxide prepared in this way (ammoniacal silver nitrate) is treated with formaldehyde, it is reduced to metallic silver.

$$Ag_2O + H.CHO = 2Ag + \underset{\text{Formic acid.}}{H.COOH.}$$

Experiment 14. Take about 5 c. c. of a 2 or 3 p. c. solution of silver nitrate in a test tube. Add ammonium hydrate drop by drop, till the black precipitate first formed is just dissolved. Now add to this solution a few drops of formaldehyde solution and warm. If the test tube is clean, a brilliant mirror of metallic silver is deposited on the sides of the test tube.

Formaldehyde reduces mercuric chloride first to mercurous chloride (calomel) and finally to metallic mercury.

$$2HgCl_2 + H.CHO + H_2O = Hg_2Cl_2 + H.COOH + 2HCl$$
$$Hg_2Cl_2 + H_2O + H.CHO = 2Hg + H.COOH + 2HCl$$

Formaldehyde reduces **Fehling's solution** giving a reddish brown precipitate of cuprous oxide.

For qualitative purposes, Fehling's solution is made by dissolving :—

(*a*) 4 grams of copper sulphate in 50 c. c. of water,

(*b*) 17 grams of Rochelle's salt (sodium potassium tartrate) and 6 grams of caustic soda in 50 c. c. of water, and then mixing the two solutions (*a*) and (*b*). The reaction which takes place when Fehling's solution is reduced by formaldehyde may be represented by the following equation :

$$2CuO + H.CHO = \underset{\text{cuprous oxide.}}{Cu_2O} + H.COOH.$$

Experiment 15. Take about one c.c. of Fehling's solution in a test tube and add a small quantity of formaldehyde solution and heat. A reddish brown precipitate of cuprous oxide will be deposited.

Formaldehyde directly combines with sodium bi-sulphite, and hydrocyanic acid to form addition products.

$$H{\cdot}CHO + NaHSO_3 = \begin{array}{c} H \\ | \\ H—C—OH \\ | \\ SO_3{\cdot}Na \end{array}$$ bi-sulphite compound of formaldehyde.

$$H{\cdot}CHO + HCN = \begin{array}{c} H \\ | \\ H—C—OH \\ | \\ CN \end{array}$$ Formaldehyde cyanhydrin.

It reacts with ammonia to form a complex compound, hexamethylene-tetra-amine which is also known as urotropine or hexamine.

$$6H.CHO + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

Urotropine is used in medicine as a urinary antiseptic.

Formaldehyde reacts with phenyl hydrazine ($C_6H_5NH{\cdot}NH_2$) to form a phenyl hydrazone.

$$\begin{array}{c} H \\ | \\ H—C \end{array} = \boxed{O + H_2}\, N—NHC_6H_5 =$$

$$\begin{array}{c} H \\ | \\ H—C \end{array}=N—NHC_6H_5 + H_2O.$$

It reacts with hydroxyl amine to give an oxime.

$$\begin{array}{c} H \\ | \\ H-C \end{array} = \boxed{O + H_2}\, N—OH = \begin{array}{c} H \\ | \\ H-C \end{array}=N-OH + H_2O$$

Formaldoxime

With caustic alkalies formaldehyde gives brown resinous products of unknown constitution.

A 40% solution of formaldehyde is sold in the market under the name of **Formalin.** As it is prepared by the oxidation of methyl alcohol, formalin always contains methyl alcohol as an impurity. The presence of methyl alcohol is useful because it keeps formaldehyde in solution.

Uses of Formaldehyde.—Formaldehyde works as a strong germicide and is used for the preservation of biological specimens. For the same reason it is sometimes used for disinfecting rooms.

Formaldehyde renders glue insoluble in water; it is, therefore, used in leather tanning and also in the manufacture of artificial silk.

ACETALDEHYDE, $CH_3 \cdot CHO$.

Preparation 1. When alcohol is oxidised with acidified permanganate or dichromate, acetaldehyde is produced.

$$C_2H_5.OH + O = CH_3 \cdot CHO + H_2O.$$

Experiment 16. Fit up an apparatus as shown in figure 11. Put some strong aqueous solution of sodium dichromate (about 25 p.c) in the large round bottom flask. Supply the condenser with water at a temperature between 30—50°C., and allow a mixture of concentrated sulphuric acid and alcohol (in the proportion of 3 : 2 by volume) to run slowly into the flask. Gently warm the flask. Acetaldehyde will distil over and will collect in the receiver bottles which are kept cool by ice. The condenser serves to return the vapours of water and alcohol back to the flask.

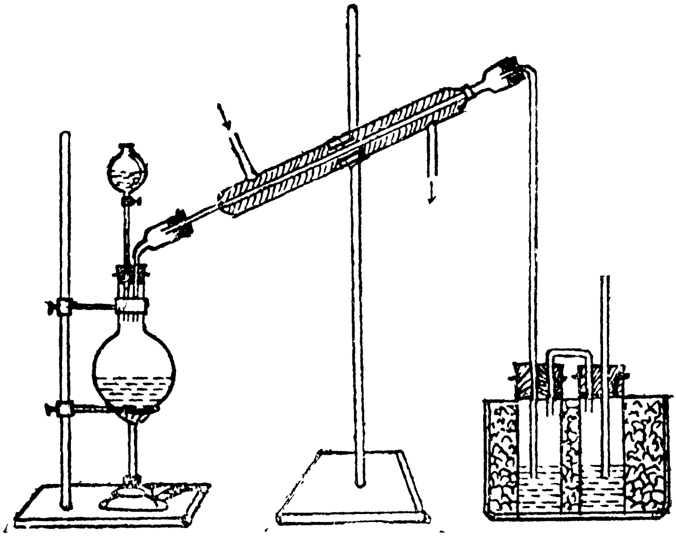


Figure 10.

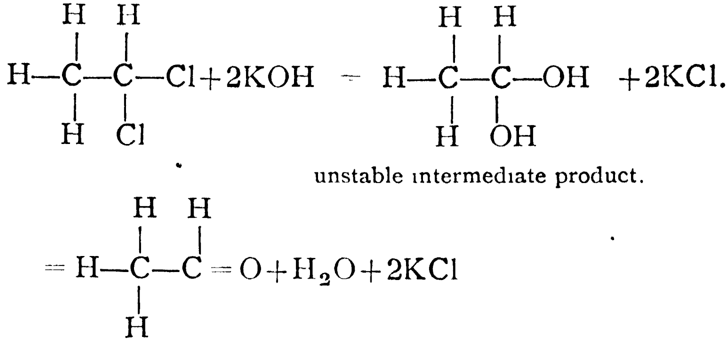
Acetaldehyde may be purified by distilling the crude aldehyde from a water bath and receiving the vapours of aldehyde in ether. The etherial solution is then saturated with ammonia gas (dry). Aldehyde ammonia separates out which is dried and distilled with dilute sulphuric acid. This gives pure acetaldehyde.

The oxidation of ethyl alcohol may also be brought about by heated copper or platinised asbestos in the presence of air.

2. When dry calcium or barium acetate is heated with dry calcium or barium formate, acetaldehyde is produced.

$$(CH_3COO)_2Ba + (H{\cdot}COO)_2Ba = 2BaCO_3 + 2CH_3{\cdot}CHO.$$

3. Ethylidene dichloride, *i. e.*, dichloroethane in which both the chlorine atoms are attached to the same carbon atom, when treated with aqueous caustic potash, gives acetaldehyde.



unstable intermediate product.

With only a few exceptions, it is observed that more than one hydroxyl group cannot remain attached to the same carbon atom. Two such groups generally react together and eliminate a molecule of water. The remaining oxygen atom attaches itself to the carbon atom by a double bond.

4. Acetaldehyde may be produced by passing acetylene through conc. sulphuric acid and adding the solution to water. The same reaction may be brought about by passing the gas through dilute sulphuric acid in the presence of mercuric oxide or mercuric sulphate.

$$C_2H_2 + H_2O = CH_3{\cdot}CHO$$

Properties. Acetaldehyde is a colourless liquid with a characteristic pungent odour. It boils at 21°C. It is very soluble in water, alcohol, and ether

In chemical properties, acetaldehyde may be taken as a true representative of the class. In its behaviour towards the following reagents it closely resembles formaldehyde :—

Oxidising agents, reducing agents, Schiff's Reagent, Fehling's solution, ammoniacal silver nitrate, sodium bisulphite, hydrocyanic acid, hydroxyl amine, caustic alkalies, and phosphorus pentachloride.

Oxiding Agents give acids.

$$H{\cdot}CHO + O = H{\cdot}COOH$$

$$CH_3{\cdot}CHO + O = CH_3{\cdot}COOH$$

Reducing agents :—Alcohols are produced.

$$H{\cdot}CHO + 2H = CH_3OH.$$

$$CH_3{\cdot}CHO + 2H = C_2H_5OH.$$

Schiff's Reagent :—Both give violet colouration.

Ammoniacal silver nitrate :—Both give a metallic mirror.

$$Ag_2O + H{\cdot}CHO = 2Ag + H{\cdot}COOH$$

$$Ag_2O + CH_3{\cdot}CHO = 2Ag + CH_3{\cdot}COOH.$$

Fehling's solution :—Both give a reddish brown precipitate of cuprous oxide.

$$2CuO + H{\cdot}CHO = Cu_2O + H{\cdot}COOH$$

$$2CuO + CH_3{\cdot}CHO = Cu_2O + CH_3{\cdot}COOH$$

Sodium bisulphite :—Both form crystalline addition products.

$$H-\overset{H \atop |}{C}=O+NaHSO_3 \quad = \quad H-\overset{H \atop |}{\underset{| \atop SO_3\cdot Na}{C}}-OH.$$

$$CH_3-\overset{H \atop |}{C}=O+NaHSO_3 \quad = \quad CH_3-\overset{H \atop |}{\underset{| \atop SO_3\cdot Na}{C}}-OH.$$

Hydrocyanic acid :—Both give additive products called cyanhydrins.

$$H-\overset{H \atop |}{C}=O+HCN \quad = \quad H-\overset{H \atop |}{\underset{| \atop CN}{C}}-OH.$$

$$CH_3-\overset{H \atop |}{C}=O+HCN \quad = \quad CH_3-\overset{H \atop |}{\underset{| \atop CN}{C}}-OH.$$

Hydroxyl amine :—Both react with the elimination of water forming aldoximes.

$$H-\overset{H \atop |}{C}=\boxed{O+H_2}N-OH = H-\overset{H \atop |}{C}=N-OH+H_2O.$$

$$CH_3-\overset{H \atop |}{C}=\boxed{O+H_2}N-OH = CH_3-\overset{H \atop |}{C}=N-OH+H_2O.$$

Phenyl hydrazine :—Both react in the same way as with hydroxyl amine forming phenyl hydrazones.

$$H-\overset{\displaystyle H}{\overset{|}{C}} = \boxed{O+H_2} N-NHC_6H_5$$

$$= H-\overset{\displaystyle H}{\overset{|}{C}}=N-NHC_6H_5+H_2O$$

$$CH_3-\overset{\displaystyle H}{\overset{|}{C}} = \boxed{O+H_2} N-NHC_6H_5$$

$$= CH_3-\overset{\displaystyle H}{\overset{|}{C}}=N-NHC_6H_5+H_2O.$$

Caustic alkalies :—Both give brown resinous products of unknown consitution.

Phosphorus pentachloride :—Both give dichloro-derivatives of paraffins.

$$H{\cdot}CHO+PCl_5 = CH_2Cl_2+POCl_3.$$

$$CH_3{\cdot}CHO+PCl_5 = \underset{\text{Ethylidene chloride}}{CH_3{\cdot}CHCl_2}+POCl_3$$

Acetaldehyde differs from formaldehyde in its action towards ammonia.—The former gives an additive compound called aldehyde ammonia,

$$CH_3-\overset{\displaystyle H}{\overset{|}{C}} = O+NH_3 = CH_3-\underset{\displaystyle NH_2}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-OH$$

while formaldehyde forms a compound known as hexamethylene tetramine which though a crystalline compound is quite different from aldehyde ammonia

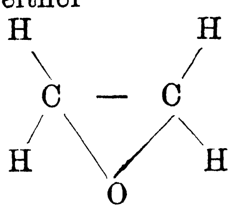
in chemical nature, and is produced with the elimination of water.

$$6H{\cdot}CHO+4NH_3 = (CH_2)_6N_4+6H_2O.$$

When treated with iodine and alkali, acetaldehyde gives iodoform. With the help of this reaction acetaldehyde may be distinguished from formaldehyde which does not give iodoform on treatment with iodine and alkali.

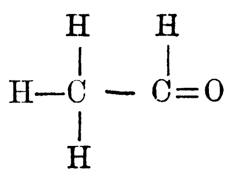
Constitution of Acetaldehyde:—Acetaldehyde is found to contain carbon, hydrogen, and oxygen. The quantitative analysis leads to the empirical formula C_2H_4O. The determination of vapour density shows that the molecular and empirical formulæ are identical.

When acetaldehyde is treated with posphorous petachloride, a compound with the formula $C_2H_2Cl_2$ (dichloroethane) is obtained which shows that the oxygen atom has been replaced by two chlorine atoms and that there is no hydroxyl group in the molecule. This further shows that the oxygen atom must be directly linked with either one or the two carbon atoms and the constitution should therefore be either



(1)
Symmetrical

or



(2)
Unsymmetrical.

The following facts are in favour of the unsymmetrical formula :—

(1) On exhaustive chlorination C_2Cl_3HO (chloral) is obtained showing that the position of one atom of hydrogen is different from those of the remaining three, which is consistent with the formula No. (2). According to formula No. (1) all the hydrogen atoms are similarly situated.

(2) The dichlorethane obtained by the action of phosphorous pentachloride on acetaldehyde is different from that which is obtained by the action of chlorine on ethylene. The former gives acetaldehyde on treatment with alkali while the latter gives glycol.

(3) When C_2Cl_3HO (chloral) as obtained in (1) above is treated with caustic soda or potash, we get cholroform

$$\begin{array}{ccccc} & & Cl & & \\ & & | & & \\ H & — & C & — & Cl \\ & & | & & \\ & & Cl & & \end{array}$$

, which shows that the molecule of acetaldehyde contains a methyl group.

Uses of Acetaldehyde.—Acetaldehyde is used in the synthesis of some artificial dyes and medicines.

Polymerisation.—When an aqueous solution of formaldehyde is evaporated formaldehyde is gradually tranformed into a white solid called **Paraformaldehyde** $(CH_2O)_2$. Similarly when liquefied formal-

dehyde is left alone, it is converted into a white substance called **Metaformaldehyde** or **Trioxymethylene** $(CH_2O)_3$. The molecular weight of paraformaldehyde is twice while that of metaformaldehyde is thrice the molecular weight of formaldehyde. These are produced by the combination of two and three molecules of formaldehyde respectively.

Such a change where two or more molecules of a substance combine to form a molecule of another substance is known as **polymerisation**, and the new substance is known as the **polymer** of the original substance.

Ecetaldehyde also undergoes polymerisation. When a drop of conc. sulphuric acid is added to acetaldehyde, it rapidly polymerises to form a substance called paraldehyde $(C_2H_4O)_3$. Paraldehyde is used in medicine as a saporofic. It is colourless, pleasant smelling but poisonous liquid. It boils at 124°C. Distilled with sulphuric acid it is converted into acetaldehyde again. It does not possess any of the properties of acetaldehyde.

Metaldehyde is another polymer of acetaldehyde and is produced by the action of acids on actaldehyde at low temperatures. It is a colourless crystalline solid. It also does not share any of the properties of acetaldehyde.

When acetaldehyde is treated with dilute hydrochloric acid, potassium carbonate, or zinc chloride,

a substance called **aldol** is produced by the combination of two molecules of the aldehyde.

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO = \begin{array}{c} \quad\quad H \\ \quad\quad | \\ CH_3—C—CH_2{\cdot}CHO \\ \quad\quad | \\ \quad\quad OH \end{array}$$

aldol

This change is known as **aldol condensation.** Aldol is a colourless liquid and possesses all the properties of aldehydes.

When a mixture of acetaldehyde and ethyl alcohol is heated to about 100°C., **acetal** is formed.

$$CH_3CHO + 2C_2H_5{\cdot}OH = CH_3{\cdot}CH{:}(OC_2H_5)_2 + H_2O$$

ACETONE. $CH_3—CO—CH_3$.

Preparation 1. It was mentioned in connection with the products of wood distillation, that acetone is one of those products.

2. When secondary propyl alcohol is oxidised. acetone is formed.

$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H— & C & — & C & — & C & —H \\ & | & & | & & | & \\ & H & & OH & & H & \end{array} + O = \begin{array}{ccccccc} & H & & & & H & \\ & | & & & & | & \\ H— & C & — & C & — & C & —H \\ & | & & \| & & | & \\ & H & & O & & H & \end{array} + H_2O.$$

Secondary propyl alcohol — acetone

As in the case of primary alcohols, this oxidation takes place by the removal of two atoms of hydrogen

—one from the—OH group and the other from that carbon atom to which the hydroxyl group is attached. The middle carbon atom is converted into a **carbonyl group** ($=CO$), the two valencies of which are satisfied by two different carbon atoms.

3. When dry calcium acetate is heated, acetone is produced.

$$(CH_3{\cdot}CO{\cdot}O)_2Ca = CH_3{\cdot}CO{\cdot}CH_3 + CaCO_3.$$

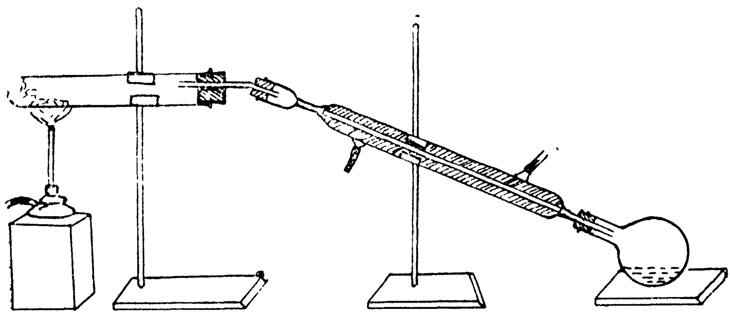


Fig. 11.

Experiment 17. Fit up an apparatus as shown in the Figure 11. Take some dry calcium acetate in the hard glass test tube and heat carefully. Acetone will collect in the receiver.

4. If the dichloropropane in which the two chlorine atoms are attached to the middle carbon atom, is treated with aqueous caustic potash, acetone is produced.

$$CH_3{\cdot}CCl_2{\cdot}CH_3 + 2KOH = CH_3{-}\underset{\displaystyle OH}{\overset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}}{-}CH_3 + 2KCl$$

Unstable intermediate product.

$$= CH_3—CO—CH_3 + 2KCl + H_2O.$$

During war time for military purposes large quantities of acetone were produced from maize starch by a biochemical method.

By comparing methods No. 2, 3, and 4, with the corresponding methods of the preparation of acetaldehyde, it will be clear that they are analogous.

Properties. Acetone is a colourless volatile liquid, with a characteristic odour. It boils at 56°C. It burns with a non-luminous flame. It is a very good solvent for many organic substances. It is miscible with water in all proportions.

There is a close resemblance between acetone and acetaldehyde in some of their properties. The resemblance is due to the presence of the carbonyl group in both the molecules.

The following may be taken as the typical points of resemblance between the two substances :—

1. On reduction both the substances give alcohol :

$$CH_3{\cdot}CHO + 2H = \underset{\text{ethyl alcohol.}}{CH_3{\cdot}CH_2{\cdot}OH.}$$

$$CH_3{\cdot}CO\,CH_3 + 2H = \underset{\text{isopropyl alcohol.}}{CH_3{\cdot}CH\,(OH){\cdot}CH_3.}$$

2. On oxidation they give acids :

$$CH_3{\cdot}CHO + O = CH_3{\cdot}CO.OH.$$

$$CH_3{\cdot}CO{\cdot}CH_3 + 2O_2 = CH_3{\cdot}CO{\cdot}OH + CO_2 + H_2O.$$

3. Both the substances form additive compounds with sodium bisulphite :

$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O+NaHSO_3 \quad = \quad CH_3-\underset{\underset{\displaystyle SO_3.Na}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH.$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O+NaHSO_3 \quad = \quad CH_3-\underset{\underset{\displaystyle SO_3.Na.}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH.$$

This reaction is utilised for the purification of acetone. Impure acetone is treated with a concentrated solution of sodium bisulphite whereby the bisulphite compound crystallises out which is separated and pressed to remove the adhering liquid and then distilled with sodium carbonate.

$$2(CH_3)_2 : C(OH).SO_3.Na+Na_2CO_3 = 2\,(CH_3)_2 : CO$$
$$+2Na_2SO_3+CO_2+H_2O.$$

4. Both form additive compounds with hydrocyanic acid :

$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O+HCN \quad = \quad CH_3-\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH.$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O+HCN \quad = \quad CH_3-\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH.$$

On the careful examination of reactions 3 and 4, it will be observed that these reactions depend upon the breakage of the double bond between carbon and oxygen atoms of the carbonyl group. When the double bond breaks, one valency of each of the two atoms becomes free. The oxygen atom takes up an atom of hydrogen from the reacting substance and is converted into a hydroxyl group. The carbon atom joins with the remaining portion of the molecule of the reacting substance.

The following reactions depend upon the removal of the oxygen atom of the carbonyl group in the form of water.

5. With hydroxyl amine they form oximes:

$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=\boxed{O+H_2}N-OH =$$

$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=N-OH+H_2O$$

Acetaldoxime.

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=\boxed{O+H_2}N-OH =$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=N-OH+H_2O.$$

Acetoxime.

6. They give phenyl hydrozones when they are treated with phenyl hydrazine.

$$CH_3-\overset{\displaystyle H \atop |}{C}=\boxed{O+H_2}N-NH.C_6H_5 =$$

$$CH_3-\overset{\displaystyle H \atop |}{C}=N-NH.C_6H_5+H_2O.$$

$$CH_3-\overset{\displaystyle CH_3 \atop |}{C}=\boxed{N+H_2}N-NH.C_6H_5 =$$

$$CH_3-\overset{\displaystyle CH_3 \atop |}{C}=N-NH.C_6H_5+H_2O.$$

7. Phosphorus pentachloride (PCl_5) replaces the oxygen atom by two chlorine atoms.

$$CH_3{\cdot}CHO+PCl_5 = CH_3{\cdot}CHCl_2+POCl_3$$
$$CH_3{\cdot}CO{\cdot}CH_3+PCl_5 = CH_3{\cdot}CCl_2{\cdot}CH_3+POCl_3$$

No hydrogen chloride is evolved in this reaction (distinction from alcohol.)

Points of difference between the properties of acetaldehyde and acetone.

1. On reduction acetaldehyde gives a primary alcohol while acetone gives a secondary alcohol.

2. On oxidation the aldehyde gives the acid with the same number of carbon atoms, while in the case of acetone, the carbon chain breaks and an acid with a smaller number of carbon atoms is obtained.

3. Acetaldehyde reacts with ammonia to form

a crystalline compound, while acetone forms some complex compounds.

4. Acetaldehyde gives a violet colour with Schiff's reagent while acetone does not react.

5. Acetaldehyde reduces ammoniacal silver nitrate and Fehling's solution while acetone does not work as a reducing agent.

6. Acetaldehyde undergoes polymerisation, while acetone does not polymerise.

7. Acetaldehyde forms a brown resinous product with caustic alkalies, while acetone does not react.

Uses of Acetone.—Acetone is used as a solvent for acetylene, celluloid and many other organic substances. It is employed in the manufacture of iodoform and chloroform.

Aldehydes and Ketones.—A primary alcohol, when oxidised is converted into an aldehyde. Aldehydes are substances which contain the monovalent group—CHO which is known as the aldehydic group.

Secondary alcohols give rise to ketones. Both aldehydes and ketones contains the carbonyl group (=CO). All the aldehydes behave like acetaldehyde, while all the ketones behave like acetone.

CHLORAL. $CCl_3.CHO$.

When ethyl alcohol is treated with chlorine, it is first oxidised to acetaldehyde, and then chlorine works as a substituent forming chloral.

$$C_2H_5.OH + Cl_2 = CH_3\,CHO + 2HCl.$$
$$CH_3.CHO + 3Cl_2 = CCl_3.CHO + 3HCl.$$

Chloral is a heavy oily liquid. It boils at 97°C. It possesses all the fundamental properties of aldehydes.

Warmed with caustic soda or caustic potash, it gives chloroform :

$$\begin{array}{c} CCl_3 \\ | \\ H-C=O \end{array} + \begin{array}{c} H \\ | \\ OK \end{array}$$
$$= CHCl_3 + \underset{\text{Potassium formate.}}{H.CO.OK.}$$

A similar reaction takes place when chloroform is prepared by heating together bleaching powder and alcohol. By the action of chlorine, the alcohol is converted into chloral, which reacts with calcium hydroxide of bleaching powder giving chloroform and calcium formate.

When acetone is used in place of ethyl alcohol in the preparation of chloroform, similar reactions take place. Chlorine gives trichloracetone which reacts with the alkali to give chloroform and acetate.

$$CH_3{\cdot}CO\,CH_3 + 3Cl_2 = \underset{\text{trichloracetone.}}{CCl_3{\cdot}CO{\cdot}CH_3} + 3HCl.$$

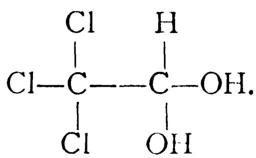
$$\begin{array}{c} CCl_3 \\ | \\ CH_3.C=O \end{array} + \begin{array}{c} H \\ | \\ ONa \end{array} = CHCl_3 + CH_3.CO.ONa.$$

The chemistry of the formation of iodoform is essentially the same as that of chloroform.

Chloral combines with water to form a colourless, crystalline, soluble substance called **chloral hydrate.**

It melts at 57°C. and is used as an antiseptic and soporific. It does not give all the reactions of aldehydes. When heated strongly, it dissociates into chloral and water. Sulphuric acid changes it into chloral.

It is believed that chloral hydrate is one of the few substances which contain more than one hydroxyl group joined to the same carbon atom. Its formula is believed to be:



To Distinguish between Acetone and Ethyl alcohol. Ethyl alcohol and acetone may be distinguished by the determination of their boiling points, provided they are pure. If they are present in dilute aqueous solutions, they may be identified by the iodoform test. Ethyl alcohol gives iodoform test only if the alkali used is caustic soda, caustic potash, or sodium carbonate It does not give iodoform with ammonia and iodine. Acetone gives iodoform even with ammonia and iodine.

Experiment 18. Take dilute solutions of acetone and ethyl alcohol in two separate test tubes. Add iodine solution to both the test tubes, followed by ammonium hydrate. A black precipitate owing to the formation of nitrogen iodide will be observed. Warm gently. Yellowish precipitate will be formed in the test tube containing acetone while no iodoform will be produced in the test tube containing ethyl alcohol.

EXERCISES ON CHAPTER X.

1. Write down the full constitutional formulæ of the following substances :

(a) Formaldehyde. (b) Acetaldehyde.
(c) Acetone. (d) Acetal.
(e) Chloral. (f) Chloral hydrate.

2. Compare in a tabular form : acetone and acetaldehyde, with regard to their methods of preparation and chemical properties.

3. What is formalin ? What are its uses ?

4. How do the following substances react with acetaldehyde and acetone :

(a) Phenyl hydrazine. (b) Hydroxyl amine.
(c) Schiff's reagent. (d) Ammoniacal silver nitrate.
(e) Caustic soda. (f) Sodium bisulphite.
(g) Hydrocyanic acid. (h) Conc. Sulphuric acid ?
(i) Phosphorus Pentachloride.

5. How will you distinguish between alcohol and acetone, when they are supplied in the form of dilute aqueous solution ?

6. What is "polymerisation" ? Illustrate your answer with concrete examples.

7. What happens when :

(a) Calcium formate is heated,
(b) Calcium acetate is heated with calcium formate,
(c) Calcium acetate is heated alone ?

Give equations.

8 How is chloral hydrate prepared ? What are its properties ?

9 A substance is known to contain a ketone mixed up with impurities. How will you proceed to isolate it in a pure form ?

10. Acetone and methyl alcohol mixed together in about equal proportions are given to you How would you separate the two ?

11. An aqueous solution contains acetaldehyde, ethyl alcohol or acetone. How would you identify the compound present ?

12. How is pure acetaldehyde prepared ? Describe its properties and draw the sketch of the apparatus used.

13. You are given three liquids and told that amongst them you will find ethyl alcohol, ether, and formaldehyde. How would you proceed to identify them ?

CHAPTER XI.

FATTY ACIDS

A homologous series of compounds containing the elements carbon, hydrogen and oxygen with the general formula $C_nH_{2n}O_2$, is classed as **fatty acids**. The characteristic group of the series is the monovalent **carboxyl group** ($-CO.OH$). It is the hydrogen of the carboxyl group which is replaceable by a metal.

They are known as fatty acids because most of them occur in fats and oils.

FORMIC ACID. H.CO.OH.

Formic acid occurs in the stings of some insects (*e. g.* ants) and also in the bristles of some nettles (*e. g.* Bichhu Ghas).

Preparation. 1. It may be obtained by the hydrolysis of hydrocyanic acid.

$$HCN + 2H_2O = \underset{\text{Ammonium formate.}}{H{\cdot}CO{\cdot}ONH_4}.$$

From ammonium formate the acid may be obtained by distillation with *dilute* sulphuric acid.

2. When boiled with caustic potash, chloroform and iodoform give potassium formate from which formic acid may be obtained by distillation with dilute sulphuric acid.

$$H-C\left\langle\begin{array}{|c|l}I+K & OH\\ I+K & OH\\ I+K & OH\end{array}\right. = H-C\left\langle\begin{array}{l}OH\\ OH\\ OH\end{array}\right. + 3KI =$$

unstable intermediate product.

$$H.CO.OH + H_2O + 3KI.$$

$$H.CO.OH + K.OH = H.CO.OK + H_2O.$$

$$H.CO.OK + H_2SO_4 = H.CO.OH + KHSO_4.$$

3. When methyl alcohol is oxidised, it is converted first into formaldehyde and then into formic acid :

$$CH_3.OH + O = H.CHO + H_2O.$$

$$H{\cdot}CHO + O = H{\cdot}CO{\cdot}OH.$$

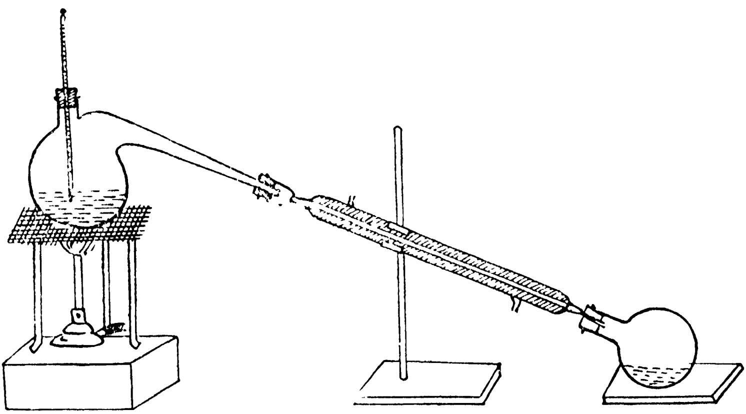


Fig. 12.

4. It is prepared by heating crystallised oxalic acid with glycerol (glycerine) to 100—110°C.

Experiment 19. A mixture of oxalic acid and glycerine in equal proportion is heated in a retort which is connected to a condenser and receiver as shown in the figure. The temperature is

maintained between 100-110°C. Carbon dioxide is evolved and formic acid begins to distil over.

The same quantity of glycerol can convert a large amount of oxalic acid into formic acid. If more acid is required more oxalic acid may be added to the same quantity of glycerol contained in the retort. The reactions which take place are complex but the final change may be represented thus:

$$\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array} = H.CO.OH + CO_2.$$

5. Formic acid may also be prepared by the direct combination of carbon monoxide and caustic potash:

$$CO + KOH = H{\cdot}CO{\cdot}OK.$$

$$H{\cdot}CO{\cdot}OK + H_2SO_4 = H.CO.OH + KHSO_4.$$

To purify formic acid, the impure acid is boiled with excess of lead carbonate and filtered. On cooling, the filtrate gives out crystals of lead formate. These crystals are dried and heated to about 100°C in a current of hydrogen sulphide (H_2S). Formic acid distils over and collects in the receiver.

$$\underset{\text{Lead formate.}}{(H{\cdot}COO)_2Pb} + H_2S = 2H{\cdot}CO{\cdot}OH + PbS.$$

Properties. Formic acid is a colourless liquid with a punget odour. It boils at 100°C. It is heavier than water (sp. gr. 1·22). It is a strong acid. Like all the other fatty acids it is monobasic.

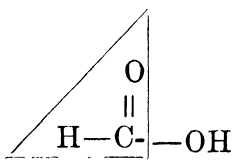
The free acid or its salts, when heated with conc. sulphuric acid, evolve carbon monoxide.

$$H{\cdot}CO{\cdot}OH = CO + H_2O.$$

The function of sulphuric acid is simply to take away elements of water from the molecules of formic acid.

Experiment 20. Take a small quantity of sodium formate in a dry test tube. Add con. sulphuric acid and warm. Apply flame to the mouth of the test tube. Carbon monoxide will burn with a blue flame.

Formic acid reduces silver nitrate to give a black precipitate of metallic silver. On examining the constitutional formula of formic acid, it will be observed, that its molecule contains an aldehyde group (—CHO). Owing to the presence of this group it works as a reducing agent.



This group is absent in all the higher fatty acids, (*e. g.* acetic acid) and consequently they do not reduce.

Formates give a red colouration with ferric chloride. The above three properties together may be taken as the distinguishing tests of formic acid.

Most of the formates are soluble in water. Silver formate and lead formate are sparingly soluble. They may be obtained by treating the acid with oxides, hydroxides, or carbonates of the metals.

Uses of Formic acid. It is a very strong germicide. It is used in dyeing and tanning works. It is used in medicine for rheumatic patients.

Rheumatism was some times cured by making the patient suffer the stings of red ants.

ACETIC ACID. $CH_3{\cdot}CO{\cdot}OH$.

Acetic acid is the next higher homologue of formic acid.

Preparation. 1. The isolation of pure acetic acid from the products of wood distillation has already been described.

2. As formic acid is obtained by the hydrolysis of hydrogen cyanide, similarly acetic acid may be obtained by the hydrolysis of methyl cyanide ($CH_3.CN$, acetonitrile).

$$CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}CO{\cdot}ONH_4.$$

$$2CH_3.CO.ONH_4 + H_2SO_4 = 2CH_3.CO.OH + (NH_4)_2SO_4.$$

Through the help of this reaction, methyl alcohol may be converted into acetic acid.

$$CH_3.OH \xrightarrow{PCl_5} CH_3.Cl \xrightarrow{HCN} CH_3.CN \xrightarrow{H_2O}$$

$$CH_3CO.ONH_4 \xrightarrow{H_2SO_4} CH_3.CO.OH.$$

3. Like formic acid, acetic acid may be prepared by the oxidation of the corresponding alcohol (ethyl alcohol) or aldehyde (acetaldehyde).

$$C_2H_5.OH+O = CH_3.CHO+H_2O.$$
$$CH_3.CHO+O = CH_3.CO.OH.$$

This process is commercially employed for the preparation of vineger (*sirka*). Vinegar is a dilute solution of acetic acid containing some other substances for flavour. When weak alcoholic drinks are left alone in contact with air, they turn sour. This change is brought by the bacteria called *mycoderma aceti*, which are present in the atmosphere, and enter the liquor. These bacteria multiply in weak alcoholic solution in the presence of air, and bring about the oxidation of ethyl alcohol. Strong alcoholic solutions cannot be fermented in this way, because the bacteria cannot survive in the presence of strong alcohol.

In the German **Quick Vinegar Process** for the conversion of weak alcoholic solutions into vinegar. the alcoholic solution is made to trickle on *birch wood* twigs which are impregnated with mother of vinegar which contains mycoderma aceti. Arrangements are made to allow sufficient air into the vessel. The dilute alcoholic solution is quickly converted into a solution of acetic acid and collects at the bottom.

Vinegar is too weak (4 to 10%) to be worked for the preparation of commercial acetic acid. Acetic acid of commerce is generally obtained from pyroligneous acid of wood distillation.

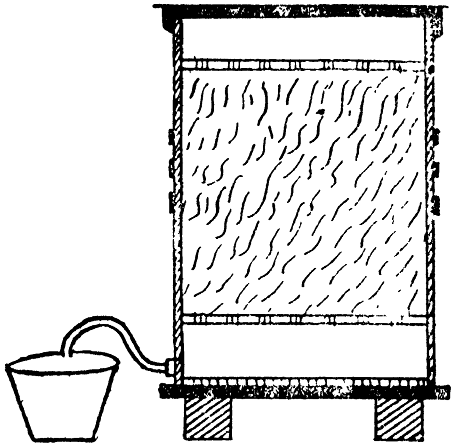


Fig. 13.

Properties. Acetic acid is a colourless, corressive liquid. It melts at 17°C and boils at 118°C. It possesses a characteristic punget odour and is miscible with water in all proportions. It is hygroscopic. It dissolves many organic substances. Unlike formic acid, it has no aldehyde group in the molecule, and possesses no reducing properties.

It is a monobasic acid. It is *weaker* than formic acid, but *stronger* than carbonic acid.

When **chlorine** is passed through acetic acid one, two or all the three atoms of hydrogen of the methyl group are replaced by chlorine, forming mono-, di-, or tri-chlor-acetic acid.

$$CH_3.CO.OH + Cl_2 = CH_2Cl.CO.OH + HCl.$$

(Solid ; M. P. 63° : B. P. 187°).

$$CH_2Cl.CO.OH + Cl_2 = CHCl_2.CO.OH + HCl.$$

(Liquid , B. P. 191°).

$$CHCl_2.CO.OH + Cl_2 = CCl_3.CO.OH + HCl.$$

(Solid, M. P. 55°, B. P. 165°).

When **phosphorous pentachloride** is added to acetic acid, the hydroxyl group contained in the carboxyl group of the acid is replaced by chlorine, exactly in the same way as ethyl chloride is produced from ethyl alcohol. The resulting product is known as acetyl chloride.

$$CH_3CO.OH + PCl_5 = CH_3.CO.Cl + POCl_3 + HCl.$$

$$C_2H_5OH + PCl_5 = C_2H_5.Cl + POCl_3 + HCl.$$

Constitution of Acetic acid.—The empirical formula is CH_2O and the molecular formula is $C_2H_4O_2$.

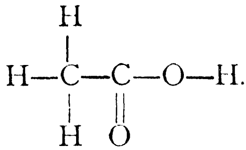
1. The molecule of acetic acid contains four hydrogen atoms but out of these only one is replaced by metal. The acid is monobasic. This shows that this hydrogen atom has a position which is different from those of the remaining three.

2. Treatment with phosphorus pentachloride gives the compound C_2H_3OCl (acetyl chloride) which clearly shows the presence of only one hydroxyl group.

3. Chlorine successively replaces three hydrogen atoms from the molecule finally giving $C_2HCl_3O_2$, which supports 1. above.

4. Formation of acetic acid by the hydrolysis of methyl cyanide (CH_3CN) and oxidation of acetaldehyde indicates the presence of a methyl group in the molecule.

Correlating all the above facts the arrangement of atoms in the molecule of acetic acid is believed to be



Uses of Acetic acid. Acetic acid is used in chemical laboratories as a reagent and also in the manufacture of synthetic dyes and artificial essences. Vinegar is used for table purposes and also in the manufacture of white lead (basic lead carbonate, *safeda*).

Acetates. All the normal acetates are soluble in water. Iron, aluminium, and chromium acetates are used as mordants in dyeing and calico printing. Sugar of lead is the normal acetate of lead.

Other Acids of the Series. The higher fatty acids closely resemble acetic acid in their chemical properties. Acetic acid may be taken as the representative of the class. Many of the higher fatty acids occur in fats and oils.

$C_2H_5.CO.OH.$	Propionic acid.
$C_3H_7.CO.OH.$	Butyric acid.
$C_{15}H_{31}.CO.OH.$	Palmitic acid.
$C_{17}H_{35}.CO.OH.$	Stearic acid.

EXERCISES ON CHAPTER XI.

1. Write down the full constitutional formulæ of the following:--

(a) Formic acid	*(b)* Acetic acid.
(c) Carboxyl group.	*(d)* Carbonyl group.
(e) Sodium formate.	*(f)* Potassium acetate.
(g) Calcium formate.	*(h)* Calcium acetate.

2. What are the different methods by which formic acid can be obtained? How can formic acid be purified?

3 How is acetic acid manufactured?

4. What is vinegar? How is it prepared? How can you get a pure sample of acetic acid from vinegar?

5. Out of all the fatty acids, only formic acid possesses reducing properties How do you account for this peculiar behaviour of formic acid?

6 How will you distinguish between a formate and an acetate?

7. You are supplied with methyl alcohol. How can you convert it into acetic acid?

8. Starting from vinegar, how will you prepare

(a) glacial acetic acid,

(b) marsh gas,

and *(c)* acetone?

9. How can a pure anhydrous sample of formic acid be prepared in the laboratory? In what respects does it differ from its homologues?

10. Indicate the methods for preparing the following substances from acetic acid —

(a) acetaldehyde,

(b) acetamide,

(c) methane.

Give the structural formula of each.

11. Describe a method for preparing formic acid and compare its properties with those of acetic acid.

12. Why can we not take formic acid as a representative of fatty acids?

13. How can acetic acid be obtained from acetylene?

CHAPTER XII.

Acetyl chloride, Acetic anhydride and Acetamide.

Acid chlorides are substances which are obtained by the replacement of the hydroxyl groups of the acids, by chlorine.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH.$$

Acetic acid.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl.$$

Acetyl chloride

$$C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH.$$

Propionic acid

$$C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-Cl.$$

Propionyl chloride.

The acid chloride of formic acid is unknown. When formic acid is treated with phosphorus chlorides, formyl chloride is probably produced but decomposes immediately to give carbon monoxide and hydrogen chloride.

$$H.CO.OH+PCl_5 = H.CO.Cl+POCl_2+HCl.$$

$$H.CO.Cl = CO+HCl.$$

Adding

$$H.CO.OH+PCl_5 = CO+POCl_3+2HCl.$$

ACETYL CHLORIDE. $CH_3 \cdot CO \cdot Cl$.

Acetyl chloride is the first member of the series, and it may be taken as the representative of the class.

Preparation. Acetyl chloride is prepared by the action of phosphorus trichloride or penetachlride on glacial acetic acid or the alkali acetates.

$$3CH_3CO.OH + 2PCl_3 = 3CH_3CO.Cl + 3HCl + P_2O_3.$$

$$CH_3.CO.ONa + PCl_5 = CH_3.CO.Cl + POCl_3 + NaCl.$$

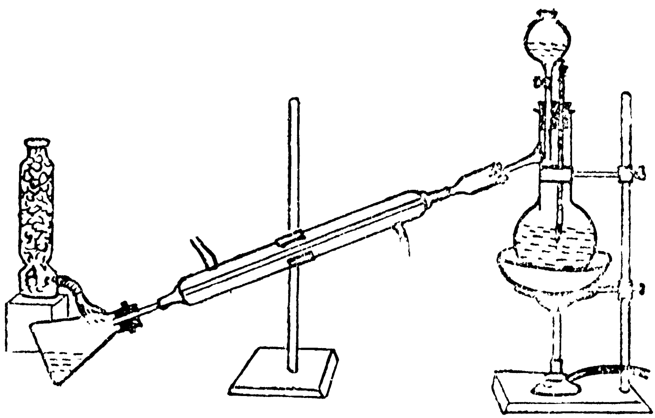


Figure 14.

Experiment 21. Fit up an apparatus as shown in the figure. In the distilling flask take about 30 grams. of glacial acetic acid and slowly run into this about 25 grams of phosphorus trichloride from the tap-funnel Hydrogen chloride is briskly evolved and the flask is gently warmed in a water bath to about 40—50°C. When the evolution of HCl has subsided, the water bath is heated to boiling. Acetyl chloride distils over and collects in the receiver. The soda-lime tower absorbs hydrogen chloride gas.

Properties. Acetyl chloride is a colourless corrosive liquid, possessing a strong, pungent, and suffocating odour. It boil at 55°C. It is heavier than water (sp. gr. 1·13). It fumes in air and is hygroscopic.

Acetyl chloride is less stable than the alkyl chlorides and is decomposed by water very quickly at ordinary temperatures.

$$CH_3.CO.\boxed{Cl + H}.O.H = CH_3.CO.OH + HCl.$$

With **caustic soda** it gives sodium acetate.

$$CH_3.CO.\boxed{Cl + Na}—OH = CH_3.CO.OH + NaCl.$$

$$CH_3.CO.OH + NaOH = CH_3.CO.ONa + H_2O.$$

With **ethyl alcohol**, ethyl acetate is produced.

$$CH_3.CO.\boxed{Cl + H}.O—C_2H_5 = CH_3.CO.OC_2H_5 + HCl.$$

When acetyl chloride is treated with **sodium ethylate,** ethyl acetate is formed.

$$CH_3.CO.\boxed{Cl + Na}—O—C_2H_5 = CH_3CO.OC_2H_5 + NaCl.$$

With **ammonia,** acetyl chloride forms acetamide.

$$CH_3.CO.\boxed{Cl + H}NH_2 = CH_3.CO.NH_2 + HCl.$$

With **sodium acetate,** it forms acetic anhydride.

$$CH_3.CO.\boxed{Cl + Na}O.CO.CH_3 = CH_3.CO.O.CO.CH_3 + NaCl.$$

When acetyl chlorids is **reduced with sodium amalgam,** it is converted into acetaldehyde.

$$CH_3.CO.\boxed{Cl + H}H = CH_3.CHO + HCl.$$

Homologues of Acetyl chloride. Formyl chloride (H.CO.Cl) is unknown. The higher homologues are prepared in the same way and possess similar properties as acetyl chloride. As the groups $—CH_3$, $—C_2H_5$ etc., are together known as alkyl radicals, similarly the groups $CH_3.CO—$, $C_2H_5.CO—$etc., are together known as **acyl radicals** and the acid chlorides

are also known as **acyl chlorides.** The general formula of the acid chlorides is represented as R CO Cl, where R represents the usual alkyl group.

Comparison of Ethyl chloride and Acetyl chloride.

1. **State:** Ethyl chloride is a gas at ordinary temperatures the liquid boils at 12°C. Acetyl chloride is liquid B. P. 55°C.

2. **Colour:** Both are colourless,

3. **Odour:** Ethyl chloride possesses fragrant smell while acetyl chloride has a pungent suffocating odour.

4. **Action of water:** In both cases the chlorine atom is replaced by a hydroxyl group.

$$C_2H_5.\boxed{Cl+H}—OH = C_2H_5.OH+HCl.$$

$$CH_3.CO.\boxed{Cl+H}—OH = CH_3.CO.OH+HCl.$$

Ethyl chloride gives ethyl alcohol while acetyl chloride gives acetic acid.

5. **Action of caustic soda:** The two molecules combine together with the elimination of sodium chloride. Ethyl chloride gives ethyl alcohol while acetyl chloride produces acetic acid in the same way as with water.

$$C_2H_5.\boxed{Cl+Na}—OH = C_2H_5.OH+NaCl.$$

$$CH_3CO.\boxed{Cl+Na}—OH = CH_3.CO.OH+NaCl.$$

6. **Action of ethyl alcohol:** Ethyl chloride does not react with alcohol, while acetyl chloride gives ethyl acetate.

$$CH_3CO.\boxed{Cl+H}—O.C_2H_5 = CH_3.CO.OC_2H_5+HCl.$$

7. **Sodium ethylate:** Both substances react in the same way. Ethyl chloride gives ether while acetyl chloride gives ethyl acetate.

$$C_2H_5|Cl+Na|-O.C_2H_5 = C_2H_5-O-C_2H_5+NaCl.$$

$$CH_3CO|Cl+Na|-O\,C_2H_5 = CH_3.CO.OC_2H_5+NaCl.$$

8. **Action of Sodium acetate:** Sodium chloride is eliminated as in the previous reaction and the remaining portions of the two molecules join together. Ethyl chloride gives ethyl acetate and acetyl chloride gives acetic anhydride.

$$C_2H_5.Cl+CH_3.CO.ONa. \quad CH_3.CO.OC_2H_5+NaCl.$$

$$CH_3.CO|Cl+Na|O.CO\,CH_3=CH_3.CO.O\,CO.CH_3+NaCl.$$

9. **Action of ammonia:** The chlorine atom is replaced by amino group ($-NH_2$).

$$C_2H_5.|Cl+H|-NH_2 \quad C_2H_5.NH_2+HCl.$$

$$CH_3.CO|Cl+H|-NH_2 = CH_3CO.NH_2+HCl.$$

10. On reduction with sodium amalgam, the chlorine is replaced by hydrogen.

$$C_2H_5.|Cl+H|\,H = C_2H_6+HCl.$$

$$CH_3CO\,|Cl+H|\,H = CH_3.CHO+HCl.$$

It will be observed that in all the above reactions ethyl chloride and acetyl chloride closely resemble one another. But the reaction in all the cases is

more energetic with acetyl chloride than with ethyl chloride.

ACETIC ANHYDRIDE. $CH_3.CO\,O.CO.CH_3$.

Acetic anhydride is the first member of the series of the compounds which are called anhydrides. Anhydride of formic acid is not known. On comparing the formula for acetic anhydride, with that of acetic acid, it will be observed that it appears to have been formed by the elimination of a molecule of water from two molecules of acetic acid.

$$\begin{array}{lcl} CH_3CO.OH. & \qquad & CH_3-C=O \\ & & \qquad\quad \diagdown O \\ CH_3\,CO.OH. & & CH_3-C=O \end{array}$$

But actually it is not prepared by the direct dehydration of acetic acid.

Preparation. As has already been mentioned in connection with the properties of acetyl chloride, acetic anhydride is obtained by the action of sodium acetate on acetyl chloride.

$$CH_3.CO|\underline{Cl+Na}|O.OC.CH_3 = CH_3.CO.O.CO.CH_3 + NaCl.$$

Experiment 22. Fit up an apparatus as shown in the figure. In the distilling flask take about 30 grams. of fused sodium acetate and add from the tap funnel about 25 grams of acetyl chloride, little by little, shaking and cooling the flask from time to time. Distill the contents of the flask on a sand bath. Acetic anhydride distills between 130-140°C.

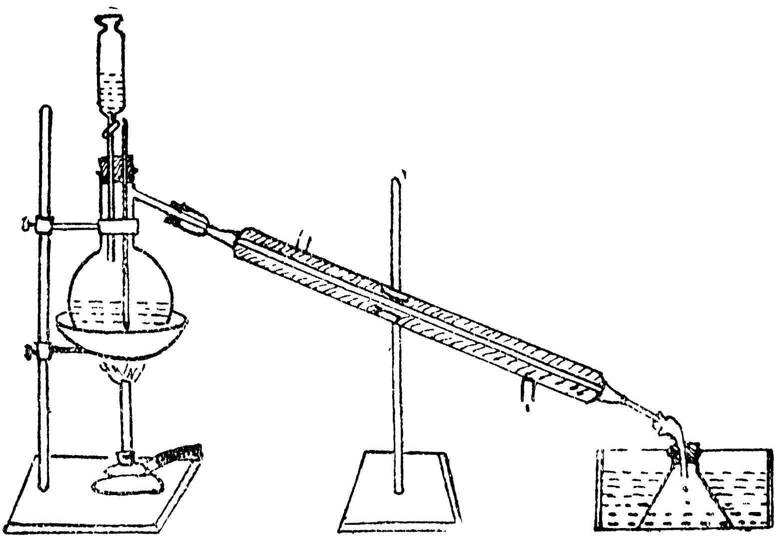


Fig. 15.

Properties. Acetic anhydride is a colourless, mobile liquid. It possesses a suffocating odour and boils at 137°C.

In chemical properties it closely resembles acetyl chloride.

With water it gives acetic acid.

$$\begin{array}{l} CH_3.CO \\ \qquad\quad \rangle O \quad + H_2O \; = \; 2CH_3.CO.OH. \\ CH_3.CO \end{array}$$

With caustic soda it gives sodium acetate.

$$\left.\begin{matrix}CH_3.CO\\ CH_3.CO\end{matrix}\right\rangle O + NaOH = CH_3.CO.ONa + CH_3.CO.OH.$$

$$CH_3.CO.OH + NaOH = CH_3.CO.ONa + H_2O.$$

With alcohol, it gives ethyl acetate.

$$\left.\begin{matrix}CH_3.CO\\ CH_3.CO\end{matrix}\right\rangle O + C_2H_5.OH = CH_3.CO.OC_2H_5 + CH_3.CO.OH$$

With sodium ethylate, ethyl acetate is produced.

$$\left.\begin{matrix}CH_3.CO\\ CH_3.CO\end{matrix}\right\rangle O + C_2H_5.ONa = CH_3.CO.OC_2H_5 + CH_3.CO\ ONa.$$

With ammonia it forms acetamide.

$$\left.\begin{matrix}CH_3.CO\\ CH_3.CO\end{matrix}\right\rangle O + 2NH_3 = CH\ \ CO.NH_2 + CH_3.CO.ONH_4$$

Acetyl chloride and acetic anhydride are the reagents of great chemical importance. They are used in the preparation of many organic compounds, and also in the estimation of the number of hydroxyl and amino groups in organic substances.

Other acid chlorides and anhydrides behave like acetyl chloride and acetic anhydride respectively.

AMIDES. $R.CO.NH_2$.

An amide is a substance the formula of which is

obtained by the replacement of the hydroxyl group of the carboxyl group of an acid by an amino-group ($-NH_2$).

$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH. \qquad\qquad H-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2.$$

Formic acid. Formamide.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH. \qquad\qquad CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2.$$

Acetic acid. Acetamide.

FORMAMIDE. $H.CO.NH_2$.

Formamide is the amide of formic acid. It is formed by the action of ammonia on ethyl formate.

$$H.CO.OC_2H_5 + NH_3 = H.CO.NH_2 + C_2H_5.OH.$$

It may also be obtained by heating ammonium formate in a sealed tube.

$$H.CO.ONH_4 = H.CO.NH_2 + H_2O.$$

Formamide is a colourless liquid boiling at about 2C0°C. At the boiling point it partially decomposes into carbon monoxide and ammonia.

$$H.CO.NH_2 = CO + NH_3.$$

ACETAMIDE. $CH_3.CO.NH_2$.

Acetamide is the amide of acetic acid and may be taken as a true representative of the class.

Preparation 1. It may be obtained by the dry distillation of ammonium acetate.

$$CH_3.CO.ONH_4 = CH_3.CO.NH_2 + H_2O.$$

Experiment 23. Melt some ammonium acetate in a porcelain dish and pour it into a distilling flask. Distil the contents of the flask using an air condenser. Collect the liquid distilling between 190-200°C. On cooling the distillate will deposit crystals of acetamide.

2. Acetamide may also be obtained by the partial hydrolysis of methyl cyanide (acetonitrile).

$$CH_3.CN + H_2O = CH_3.CO\,NH_2.$$

Complete hydrolysis gives ammonium acetate.

$$CH_3.CN + 2H_2O = CH_3.CO.ONH_4.$$

3. It may be obtained by the action of ammonia on acetyl chloride or acetic anhydride.

$$CH_3.CO.Cl + NH_3 = CH_3.CO.NH_2 + HCl$$

$$\left.\begin{array}{l}CH_3.CO\\ \\ CH_3.CO\end{array}\right\rangle O + NH_3 = CH_3.CO.NH_2 + CH_3.CO.OH.$$

4. When ethyl acetate is heated with aqueous ammonia, acetamide is produced.

$$CH_3.CO.OC_2H_5 + NH_3 = CH_3.CO.NH_2 + C_2H_5OH.$$

Properties. Acetamide is a colourless, crystalline solid. The impure substance possesses a characteristic unpleasant odour. It melts at 83°C. It dissolves readily in alcohol and water.

When it is boiled with caustic soda, it gives sodium acetate.

$$CH_3.CO.NH_2 + NaOH = CH_3.CO.ONa + NH_3.$$

This reaction may be taken as a distinguishing test between ammonium salts and acetamide. Ammonium acetate evolves ammonia even on shaking with caustic soda in the cold while acetamide is hydrolysed only on heating.

Heated with phosphorus pentoxide, it forms methyl cyanide, by the loss of a molecule of water.

$$CH_3\,CO.NH_2 = CH_3.CN + H_2O.$$

When it is treated with nitrous acid, it is converted into acetic acid with the evolution of nitrogen.

$$CH_3.CO.NH_2 + HNO_2 = CH_3.CO.OH + H_2O + N_2.$$

When acetamide is treated with bromine and caustic potash, methyl amine is produced. This reaction is known as **Hofmann's reaction.**

1. $CH_3.CO.NH_2 + Br_2 = CH_3.CO.NHBr + HBr.$
2. $CH_3.CO.NHBr + KOH = CH_3.NH_2 + CO_2 + KBr.$
3. $HBr + KOH = H_2O + KBr.$
4. $CO_2 + 2KOH = K_2CO_3 + H_2O.$

Adding equations 1, 2, 3, and 4 we get,

$$CH_3.CO.NH_2 + Br_2 + 4KOH = CH_3.NH_2 + K_2CO_3 + 2KBr + 2H_2O.$$

Unlike acetyl chloride and acetic anhydride, acetamide is not hydrolysed by water or alcohol.

Comparison of Ethyl-amine and Acetamide.

	Ethyl amine.	Acetamide.
State.	Gas.	Solid.
Solubility in water.	Soluble.	Soluble.
Action of Caustic soda.	No action.	Evolves ammonia on heating.
Action of Hydrogen chloride.	Combines directly to form the hydrochloride.	Combines directly to form a hydrochloride which is less stable.
Action of Nitrous acid.	The—NH_2 group is replaced by -OH group with evolution of nitrogen. Ethyl alcohol is produced.	The—NH_2 group is replaced by -OH group with evolution of nitrogen. Acetic acid is produced
Action with litmus.	Alkaline reaction	No alkaline reaction

EXERCISES ON CHAPTER XII.

1. What is acetyl chloride? Describe its preparation and properties.

2 How is acetic anhydride obtained? What are its properties?

3. Write down the methods of preparation and properties of acetamide.

4. How do the following substances behave towards acetyl chloride, acetic anhydride and acetamide —

Water, caustic soda, alcohol, and ammonia?

5. What happens when .

(*a*) Ammonium acetate is heated .

(*b*) Ethyl acetate is heated with strong ammonia;

(*c*) Acetamide is heated with phosphorus pentoxide,

(*d*) Acetamide is treated with bromine and caustic potash,

and (*e*) Nitrous acid is added to acetamide?

6. How will you prepare methyl alcohol from ethyl alcohol?

7. Write down the constitutional formulae of acetic anhydride, formamide, acetyl chloride, acetamide, propionyl chloride, and anhydride of propionic acid

8 By what reaciions would you obtain the following derivatives from acetic acid:

Acetyl chloride, acetamide, ethyl acetate, acetic anhydride and mono-chlor-acetic acid?

9. How can the following be differentiated from one another.—

(*a*) acetyl chloride and acetic anhydride;

(*b*) acetylene and ethylene?

10 How is acetyl chloride acted upon by eaoh of the following substances

(*i*) water, (*ii*) ethyl alcohol,

(*iii*) ammonia, (*iv*) sodium acetate?

11. How would you prepare acetyl chloride? Draw a neat sketch of the apparatus you would use and explain by means of equations the action of water, ethyl alcohol and ammonia on acetyl chloride.

12. Compare ethyl amine with acetamide.

13 Compare acetyl chloride with ethyl chloride.

14. How will you obtain (*a*) acetamide from acetic acid, (*b*) methyl, amine from acetamide, and (*c*) methyl alcohol from methyl amine? Give equations.

15. Starting from acetic acid, how can acetyl chloride be obtained? What products would you expect when acetyl chloride is acted upon by (*a*) water, (*b*) ammonia, and (*c*) sodium acetate? Give all necessary equations.

16. Describe briefly giving equations where possible, the reactions which take place between the following substances —

(*a*) a watery paste of bleaching powder and acetic acid.

(*b*) ethyl alcohol and acetic anhydride

(*c*) silver mitrate solution and formic acid

(*d*) iodoform and caustic soda

17. What happens when

(*a*) ethyl acetate and

(*b*) acetamide are boiled with caustic soda? Suggest any method by which you can separate one of the products of the reaction.

18. Indicate methods for preparing the following substances from acetic acid,—

(*a*) acetaldehyde, (*b*) acetemide, (*c*) methane.

Give the structral formula of each.

CHAPTER XIII.

ESTERS

When describing the properties of ethyl and methyl alcohols, it was pointed out that although they are neutral substances, yet in certain respects they behave like caustic soda. A metallic hydroxide reacts with an acid to form salt ond water ; similarly an alcohol reacts with an acid to form an **ethereal salt** and water.

$$NaOH + CH_3.CO.OH = CH_3.CO.ONa + H_2O.$$

$$C_2H_5.OH + CH_3.CO\ OH = CH_3.CO.OC_2H_5 + H_2O.$$

Such ethereal salts which are obtained by such an interaction of alcohols and acids are called **esters.** The acids may be organic or inorganic.

Some Esters, their Names and Formulæ.

Ethyl acetate	$CH_3.CO.OC_2H_5.$
Methyl acetate	$CH_3.CO.OCH_3.$
Ethyl formate	$H.CO.OC_2H_5.$
Ethyl propionate	$C_2H_5.CO.OC_2H_5.$
Methyl propionate	$C_2H_5.CO.OCH_3.$
Ethyl chloride	$C_2H_5.Cl.$
Ethyl nitrate	$C_2H_5.NO_3.$
Ethyl hydrogen sulphate	$C_2H_5.HSO_4.$
Di-ethyl sulphate	$(C_2H_5)_2.SO_4.$

The esters reacts with water to reproduce the original alcohol and acid.

$$CH_3.CO.OC_2H_5 + H_2O = CH_3.CO.OH + C_2H_5.OH.$$

Such a reaction in which the products of a reaction interact again to reproduce the original substances is known as **reversible reaction** and is represented thus :

$$CH_3\,CO.OH + C_2H_5.OH \rightleftarrows CH_3.CO.OC_2H_5 + H_2O.$$

One may start with the acid and the alcohol or with the ester and water, the products, as soon as they are formed will begin to react to form the original substances. To start with, the velocity of the forward change is greater than the volocity of the reverse change because the *concentration* of the original substances is greater than that of the resulting products. But as the reaction proceeds the velocity of the direct change will go on decreasing while that of the reverse change will go on increasing. A point will ultimately be reached when the two velocities will counter-balance one another. This point is known as the equilibrium point. In this particular case the forward change is known as **esterification** and the reverse change as **hydrolysis**. All this shows that in the preparation of an ester the presence of water must be avoided as far as possible otherwise the reaction will not be complete.

ETHYL ACETATE, $CH_3.CO\,OC_2H_5$.

Preparation. 1. Ethyl acetate may be prepared by the action of ethyl alcohol on acetic acid in the presence of some dehydrating agent. Concentrated sulphuric acid or hydrogen chloride gas are the

common dehydrating agents which are used in esterification. But sulphuric acid is more convenient and cheaper.

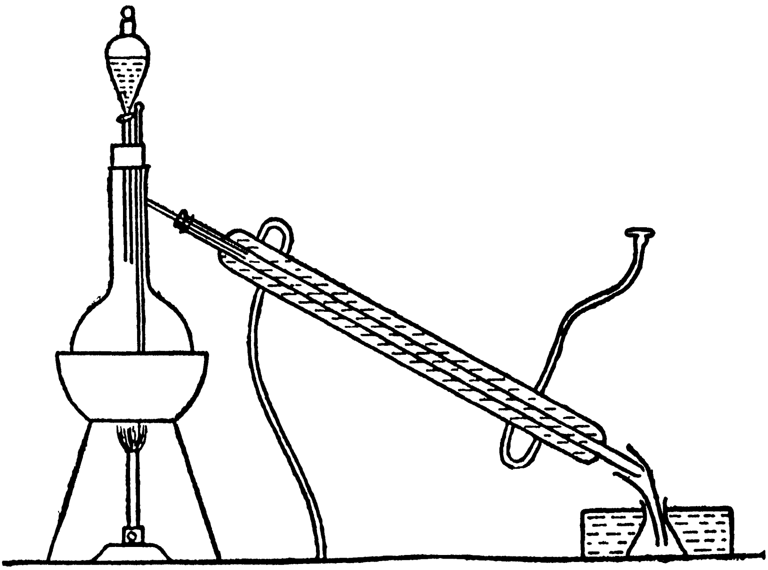


Fig. 16.

Experiment 24. Fit up an apparatus as shown in the figure. Pour a mixture of equal volumss of absolute alcohol and conc. Sulphuric acid into the flask.

Make a mixture of equal volumes of glacial acetic acid and absolute alcohol and pour it into the dropping funnel. Heat the mixture in a paraffin bath keeping the temperature at about 140°C. Add the mixture from the tap funnel almost at the same speed at which the distillation is going on.

Acetic acid, alcohol, ether, and sulphurous acid are the impurities contained in the ester produced. Wash the distillate with sodium carbonate soiution, which will remove sulphurous acid. acetic acid and alcohol. Now wash it with a little water and leave it in contact who a small quantity of fused calcium chloride Purify it by distillation.

2. Ethyl acetate is also prepared by using sodium acetate in place of acetic acid. A mixture of fused sodium acetate, concentrated sulphuric acid, and alcohol is allowed to stand overnight and distilled. Ethyl acetate will distil over which may be purified as above.

3. It may be prepared by the action of ethyl chloride on silver acetate.

$$CH_3.CO.O\boxed{Ag + Cl}—C_2H_5 = CH_3.CO.OC_2H_5 + AgCl.$$

4. When acetyl chloride is treated with alcohol or sodium ethylate, ethyl acetate is produced.

$$CH_3.CO\boxed{Cl + H}O.C_2H_5 = CH_3CO.OC_2H_5 + HCl.$$

$$CH_3.CO\boxed{Cl + Na}—O—C_2H_5 = CH_3.CO\ OC_2H_5 + NaCl.$$

5. Acetic anhydride, on treatment with alcohol or sodium alcoholate gives ethyl acetate.

$$\left.\begin{array}{l} CH_3.CO \\ CH_3.CO \end{array}\right\rangle O + C_2H_5.OH = CH_3.CO.OC_2H_5 + CH_3.CO.OH.$$

$$\left.\begin{array}{l} CH_3.CO \\ CH_3.CO \end{array}\right\rangle O + C_2H_5.ONa = CH_3.CO.OC_2H_5 + CH_3.CO.ONa.$$

Properties. Ethyl acetate is a fragrant smelling liquid insoluble in water. It boils at 77°C. It is used as a solvent for many organic substances.

When ethyl acetate is left in contact with water, it slowly hydrolyses forming acetic acid and ethyl alcohol. The hydrolysis takes place more quickly if solutions of caustic alkalies are used.

$$CH_3.CO.OC_2H_5+H_2O = CH_3.COOH+C_2H_5OH.$$

$$CH_3.CO.OC_2H_5+NaOH = CH_3.CO.ONa+C_2H_5.OH.$$

The hydrolysis of esters by boiling with caustic alkalies is known as **saponification.**

Experiment 25. Take some ethyl acetate in a round-bottomed flask. Add about double the quantity of caustic potash dissolved in water. Heat the flask on a water bath, under reflux condenser till the contents of the flask become homogeneous.

Remove the reflux and fit up an apparatus for distillation, using the same flask. Distil on the water bath. Ethyl alcohol together with some water will pass over as distillate.

Now transfer the contents of the flask to a porcelain basin. and evaporate down to dryness. The solid residue in the basin will be potassium acetate with some free alkali. Transfer this solid to a distilling flask and distil with conc. sulphuric acid. Acetic acid will distil over.

The alcohol and the acid may be identified by their usual tests.

When ethyl acetate is heated with strong ammonia it gives acetamide.

$$CH_3.CO.OC_2H_5+NH_3 = CH_3CO.NH_2+C_2H_5.OH.$$

With phosphorus pentachloride, ethyl acetate gives ethyl chloride and acetyl chloride.

$$CH_3.CO.OC_2H_5+PCl_5 = C_2H_5.Cl+CH_3.CO.Cl+POCl_3.$$

METHYL ACETATE. $CH_3.CO.OCH_3$.

Methyl acetate is an ester which may be prepared by methods which are analogous to those employed for the preparation of ethyl acetate. In its pro-

perties it closely resembles ethyl acetate. It boils at 57°C.

Other esters may similarly be prepared and possess similar properties. With only a few exceptions they are liquids insoluble in water. They are fragrant smelling and are used as artificial fruit essences.

Amyl acetate (Banana)	Iso-amyl acetate (Pear)
Ethyl butyrate (Pine apple)	Iso amyl isovelerate (Apple)

An ester is identified by resolving it into its constituent alcohol and acid by hydrolysis. The alcohol and the acid are identified by their physical properties or other special tests.

An ester may be isomeric with another ester or an acid. The isomerism will be clear from an example. The molecular formula $C_4H_8O_2$ represents the following isomeric compounds:—

$H.CO.OC_3H_7$.	Propyl formate.
$CH_3.CO.OC_2H_5$.	Ethyl acetate.
$C_2H_5.CO.OCH_3$.	Methyl propionate.
$C_3H_7.CO.OH$.	Butyric acid.

The acid can be distinguished from the esters by its solubility in caustic soda and its acid reaction. The isomeric esters can be identified separately by hydrolysing them into their alcohols and acids and then determining their properties.

Esters of Inorganic Acids. It has been mentioned

that esters are produced by the interaction of an alcohol with an acid which may be organic or inorganic. The esters of inorganic acids are the true esters and behave almost in the same way as those of the organic acids. Ethyl chloride, ethyl bromide, ethyl nitrate, ethyl hydrogen sulphate, and diethyl sulphate are the typical examples of esters of inorganic acids.

$$C_2H_5\,OH + HCl = C_2H_5.Cl + H_2O.$$
$$C_2H_5.OH + HNO_3 = C_2H_5.NO_3 + H_2O.$$
$$C_2H_5.OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O.$$
$$2C_2H_5.OH + H_2SO_4 = (C_2H_5)_2.SO_4 + 2H_2O.$$

ETHYL HYDROGEN SULPHATE. *sulphovinic acid*, $C_2H_5.HSO_4$.

This ester is prepared by heating the required quantities of conc. sulphuric acid and ethyl alcohol to about 100°C

Ethyl hydrogen sulphate being like an acid salt, forms metallic derivatives. **Its calcium and barium derivatives are soluble.** The ester may be separated from free sulphuric acid by the addition of barium carbonate. The barium derivatives being soluble will remain in solution while the insoluble barium sulphate will come out as a precipitate.

Ethyl hydrogen sulphate is very unstable substance and is very easily hydrolysed by boiling with water. If it is heated with alcohol, it forms ether.

At 0°C, ethyl alcohol reacts with sulphuric acid to form diethyl sulphate.

Salts and Esters.

Salts.	Esters.
1. Salts are substances which are produced by the interaction between bases and acids. *e.g.* $NaCl$, Na_2SO_4, $CH_3.CO.ONa$, NH_4Cl, $C_2H_5.NH_2 HCl$, etc.	1. Esters are substances that are produced by the interaction between alcohols and acids, *e.g.* $CH_3 CO.OC_2H_5$, $HCO.OC_2H_5$ $C_2H_5.HSO_4$, $(C_2H_5)_2.SO_4$, $C_2H_5.Cl$ etc.
2. The interaction between bases and acids to from salts is very rapid.	2. The interaction between alcohols and acids to form esters is very slow and reversible.
3. Salts are generally solid substances.	3. With only a few exceptions, esters are liquids.
4. Salts are generally odourless.	4. Esters are generally fragrant smelling.
5. Only a few salts hydrolyse.	5. All esters hydrolyse.
6. Almost all the salts ionise in solution, giving basic and acidic ions.	6. Esters generally do not ionise ; and if they do, their ionisation is of quite a different nature.
7. A large number of salts are soluble in water.	7. Esters are generally insoluble in water.

Oils and Fats.—Glycerine or glycerol is an alcohol, one molecule of which contains three hydroxyl groups. Fats and oils are the mixtures of glycerine esters of higher fatty acids (chiefly stearic palmitic, and oleic). Chemically speaking there is no difference between oils and fats. The semi-solid mixture of the glycerides of fatty acids is known as a fat, while a liquid mixture is called an oil. The consistency of a fat or an oil depends upon the relative quantity of the glyceride of oleic acid (an unsaturated acid) present.

The glyceride of acetic acid (glyceryl triacetate) is known as **acetin.** Similarly the glycerides that occur in fats and oils are known as **stearin, palmitin,** and **olein** etc.

$$\begin{array}{l} CH_2—OH. \\ \vert \\ CH—OH. \\ \vert \\ CH_2—OH. \end{array} \qquad \text{Glycerine or glycerol.}$$

$$\begin{array}{l} CH_2—.OOC.CH_3. \\ \vert \\ CH—OOC.CH_3. \\ \vert \\ CH_2—OOC.CH_3. \end{array} \qquad \text{Glyceryl triacetate (acetin).}$$

$$\begin{array}{l} CH_2—OOC.C_{17}H_{35}. \\ \vert \\ CH—OOC.C_{17}H_{35}. \\ \vert \\ CH_2—OOC.C_{17}H_{35}. \end{array} \qquad \text{Glyceryl tristearate (stearin).}$$

Oils and fats are insoluble in water but are soluble in some organic solvents like ether and carbon tetrachloride. The amount of an oil in seeds or oil cakes is estimated by the solvent action of these liquids.

Saponification and Soap Manufacture.—It has already been mentioned that saponification is a special term applied to the hydrolysis of esters. The term has its origin from the preparation of soaps from fats or oils. Soaps are the metallic salts of fatty acids obtained from fats or oils.

When a fat or an oil is boiled with caustic alkalies, it is hydrolysed giving glycerol and the alkali salts of the fatty acids contained in the fat or oil. Different mixtures of sodium salts of these fatty acids constitute the ordinary soap.

Experiment 26. Take some quantity of an oil (*e g.* cocoanut or cotton seed oil) in a flask Supposing it to be methyl formate which is an ester with the lowest molecular weight, calculate the quantity of caustic potash which will be required to hydrolyse it. No ester can take up more caustic potash for complete hydrolysis. Add this caustic potash dissolved in some water to the flask followed by some alcohol. Heat the flask under reflux, on the water bath till the whole solution becomes uniform. Remove the reflux and distill the c o hol.

If soap is required, add a concentrated solution of common salt to the cold contents of the flask, now transferred to a tall beaker. The soap will be "salted out," in the form of the solid salts of the fatty acids. Whatever may be the hydrolysing caustic alkali, if the soap is salted out with common salt, it will always be a sodium soap.

To get the free acids, add excess of dilute sulphuric or hydrochloric acid to the contents of the flask. The acids being insoluble will separate out. Wash these acids with water twice or thrice They may by converted into any metallic salts by dissolving them in caustic soda and adding some soluble salt of the metal, or directly from the soap. Prepare copper, lead aluminium and iron soap.

Ordinary washing soap may be obtained by thoroughly mixing in an iron pan 4 chhataks caustic soda, 4 chhataks *Besan* (बेसन), one seer water and one seer oil (ordinary rape-seed, (सरसों) oil will do). *Besan* possesses cleaning properties, and gives the required consistency to the soap.

Manufacture of Soap.—The oils or the melted fats are boiled in large iron pans by blowing in steam through the mass with 10% caustic soda. The steam keeps the mass well stirred. More caustic soda is added from time to time as is considered necessary. When the saponification is nearly complete the contents of the pan assume a darker colour. The soap is separated in a curdy state by adding a strong solution of, or dry, common salt. The mixture is boiled and allowed to settle.

The soap is boiled with water and a small quantity of alkali to ensure complete saponification. It is again salted out.

The process is sometimes repeated to obtain soap of a lighter colour. It is then run into frames and allowed to harden. The soap is then cut into slabs and bars.

The mother liquor which remains after salting out soap is known as **spent lyes**, and contains all the glycerol with a large quantity of salt, some fatty matter, and free alkali. The glycerine of commerce is obtained from this source. (See glycerol).

Waxes. Waxes are mixtures of esters of higher fatty acids and higher alcohols of methyl alcohol series. These waxes are quite different from Paraffin Wax, which is a mixture of hydrocarbons with high molecular weights.

Stearin is the glyceride of stearic acid. The stearin used in the manufacture of the so-called "stearin candles" is a misnomer, and is really a mixture of free acids obtained from fats and separated from oleic acid as far as possible. Oleic acid being liquid, will not allow the "stearin" to acquire the required hardness. Some times the oleic acid is converted into stearic acid by catalytic hydrogenation.

At present candles are made from paraffin wax.

EXERCISES ON CHAPTER XIII.

1. What are esters ? How do they differ from salts ?

2. Write down the full constitutional formulæ of the following compounds .—

Ethyl acetate, methyl acetate, ethyl formate, ethyl chloride, acetyl chloride, and acetic acid.

3 What are the different methods by which esters may be obtained ?

4. Starting from ethyl alcohol and ecetic acid, how will you obtain a pure sample of ethyl acetate ? Describe the experiment with full practical details. Give the sketch of apparatus used.

5. You are supplied with 10 grams of ethyl acetate , show how you will obtain samples of ethyl alcohol and acetic acid from this substance

6. How do ethyl and methyl acetates behave towards water, ammonia, and phosphorus pentachloride ?

7. What are fats and oils ? Describe with full practical details the isolation of soap and free acids from a sample of cotton seed oil.

What do you mean by "saponification" ? What are soaps ? Can a mixture of copper stearate, palmitate and oleate be called a soap ?

9 What are stearin, palmitin, and olein ? What is the chemical nature of stearin which is used in the manufacture of candles ?

10. How does ethyl hydrogen sulphate differ from sodium hydrogen sulphate ?

11. How could you distinguish an acid from an ester both of which had the same molecular formula $C_4H_8O_2$? How would you proceed to determine the nature of the acid and alcohol combined in an ester of the above formula ?

12. What is the action of water on the following acetic anhydride, acetamide, acetyl chloride, ethyl acetate, glacial acetic acid ?

13. *(a)* What are the typical properties of an ester? Illustrate your answer with ethyl acetate.

(b) Are the following compounds, esters or salts —

Ethyl sulphate, ethyl oxalate, ammonium acetate, methyl amine formate, sodium bicarbonate?

14. Compare the properties of the fats and soaps, and hence show how you could distinguish them experimentally.

15. What is the action of boiling aqueous solution of caustic potash on

(a) ethyl iodide, *(b)* ethyl acetate and *(c)* acetamide? Would it make any difference if alcoholic potash is used instead of aqueous potash?

16. What is the action of boiling caustic soda on a fat or an oil?

17. What are the different methods of esterification of organic acids? Illustrate your answer by means of equations

18. What is soap? What do you think of using kerosine oil to prepare it? How with the usual ingredials would you prepare soap in the laboratory.

CHAPTER XIV.

GLYCOL AND GLYCEROL

Glycol and glycerol are two of the alcohols which contain more than one hydroxyl group. Such alcohols are known as polyhydric alcohols.

ETHYLENE GLYCOL, or Glycol, $\begin{array}{l} CH_2.OH. \\ | \\ CH_2\,OH. \end{array}$

It is a dihydroxy alcohol the two hydroxyl groups of which are separately joined to the two carbon atoms. It may also be called as dihydroxy ethane. In small quantities it is formed when ethylene (C_2H_4) is oxidised with a cold dilute alkaline solution of potassium permanganate.

Glycol is prepared by heating ethylene chloride ($CH_2Cl—CH_2Cl$) or bromide with aqueous potash or soda.

$$\begin{array}{l} CH_2—\boxed{Cl+K}\,OH \\ | \\ CH_2—\boxed{Cl+K}\,OH \end{array} = \begin{array}{l} CH_2—OH \\ | \\ CH_2—OH \end{array} + 2KCl.$$

Ethylene glycol is a sweet, colourless syrupy liquid which boils at 197°C. It is freely miscible with water. With sodium, it forms a sodium derivative by the replacement of the hydrogen of the hydroxyl groups.

$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} + 2Na = \begin{array}{l} CH_2\text{—}ONa \\ | \\ CH_2\text{—}ONa \end{array} + H_2.$$

Phosphorus pentachloride gives athylene chloride, by the replacement of the two hydroxyl groups by two chlorine atoms.

$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} + 2PCl_5 = \begin{array}{l} CH_2\text{—}Cl \\ | \\ CH_2\text{—}Cl \end{array} + 2HCl + 2POCl_3.$$

Acetyl chloride or acetic anyhdride gives a diacetate.

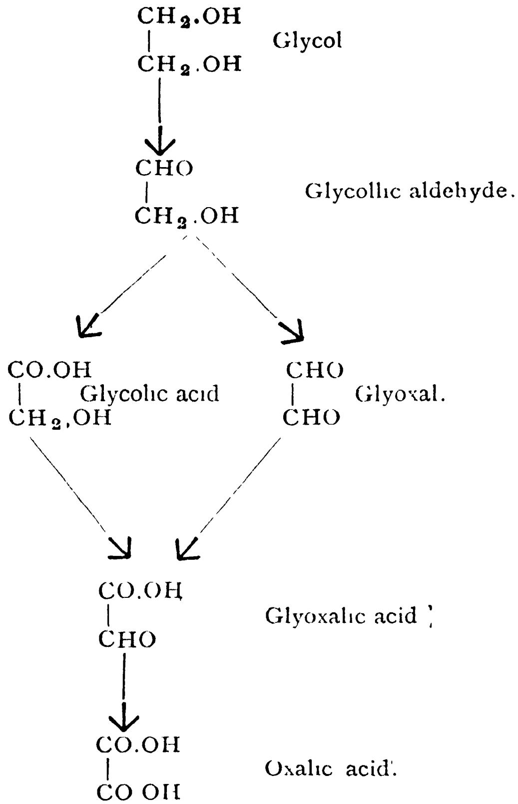
$$\begin{array}{l} CH_2\text{—}O \\ | \\ CH_2\text{—}O \end{array} \boxed{\begin{array}{l} H+Cl \\ \\ H+Cl \end{array}} \begin{array}{l} .CO.CH_3 \\ \\ .CO.CH_3 \end{array} + \begin{array}{l} CH_2.O.OC.CH_3 \\ | \\ CH._2O.OC.CH_3 \end{array} + 2HCl.$$

$$\begin{array}{l} CH_2\text{—}O \\ | \\ CH_2\text{—}O \end{array} \boxed{\begin{array}{lcr} H & & \\ & + & O \\ H & & \end{array}} \begin{array}{l} CO.CH_3 \\ \\ CO.CH_3 \end{array} = \begin{array}{l} CH_2.O.OC.CH_3 \\ | \\ CH_2.O.OC.CH_3 \end{array} + H_2O.$$

In all the above properties it resembles ethyl alcohol.

There being two alcoholic groups in the molecule of glycol, it gives many oxidation products.

Oxidation Products of Glycol.



GLYCEROL, Glycerine, or trihydroxy propane,

$$\begin{array}{l} CH_2.OH. \\ | \\ CH.OH. \\ | \\ CH_2.OH. \end{array}$$

Glycerol occurs in nature in fats and oils, which are its chief commercial sources. It is manufactured from the "*spent lyes*" of soap industry, and also from

the sweet liquors of candle industry. In addition to 8% of glycerol, the spent lyes contain free alkali, large quantities of common salt, and fatty and resinous matter.

The alkali is neutralized with acid and the liquid is filtered from fatty and resinous matter. It is then concentrated under reduced pressure, when the salts are deposited and removed. The small quantity of salts which still remains dissolved, is removed by distilling glycerol with superheated steam. Glycerine is dehydrated by evaporation in vacuo.

Pure anhydrous glycerol is a colourless crystalline solid, M. P. 17°C. Ordinarily it is a sweet, thick, syrupy liquid and is heavier than water. When pure it boils at 290°C without decomposition, but impure glycerine decomposes at its boiling point. It is hygroscopic.

When it is heated with phosphorus pentoxide or potassium hydrogen sulphate, it gives out a strong pungent odour of acrolein.

$$C_3H_5(OH)_3 = \underset{\text{Acrolein.}}{CH_2{:}CH.CHO} + 2H_2O.$$

Phosphorus pentachloride gives trichloro-propane by the replacement of the three hydroxyl groups by three chlorine atoms.

$$C_3H_5(OH)_3 + 3PCl_5 = C_3H_5Cl_3 + 3POCl_3 + 3HCl.$$

When hydrogen chloride is passed through glycerol α—monochlorhydrin is obtained.

$$\begin{array}{l} CH_2.Cl \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} \quad \alpha\text{–monochlorhydrin of glycerol}$$

But if glycerol is mixed with acetic acid and then hydrogen chloride gas is passed, $\alpha\alpha$–dichlorhydrin is obtained.

$$\begin{array}{l} CH_2.Cl \\ | \\ CH.OX \\ | \\ CH_2.Cl \end{array} \quad \alpha\alpha\text{–dichlorhydin of glycerol}$$

The third hydroxyl group cannot be replaced by chlorine simply by the action of hydrogen chloride. Phosphorus pentachloride can replace all the three.

The molecule of glycerol contains two primary and one secondary alcoholic groups; therefore a large number of oxidation products are theoretically possible, many of which are actually obtained.

If glycerol is added little by little to a well cooled mixture of nitric and sulphuric acids, and the mixture diluted with water, **trinitrate** of glycerol, or Noble's oil, $C_3H_5(NO_3)_3$, separates out as an oil. It is highly explosive, and is wrongly named as **nitroglycerin.** It is used as an explosive.

Heated with oxalic acid, glycerol gives allyl alcohol, or formic acid according as the temperature, at which the experiment is conducted, is 220° or 110°C. respectively.

Heated on a borax bead, glycerol imparts a green colour to the flame.

Tests for Glycerine. (*a*) production of acrolein when glycerol is heated with potassium hydrogen sulphate, (*b*) the borax bead test (*c*) the syrupy residue obtained when solutions of glycerol in water are heated on the water bath, may be taken as the distinguishing test of glycerol. Glycerol does not reduce Fehling's solution even after boiling with hydrochloric acid. (Distinction from grape and cane sugars).

Uses of Glycerol. The most important use of glycerol is in the manufacture of nitroglycerine which is used in the preparation of **dynamite** and **cordite**.

Dynamite is prepared by absorbing nitroglycerine by *Kieselgurh* (silicious remains of sea animals). In this form it is less dangerous.

Cordite is solid substance obtained by impregnating gun-cotton (nitrocellulos) with nitroglycerine and vaseline. When fired, it does not produce any smoke and is used in the smokeless powders.

Glycerol is used to some extent in medicine and in the manufacture of stamping inks and toilet preparations.

———

EXERCISES ON CHAPTER XIV.

1. What is glycol? How can it be prepared?

2. What is a primary alcoholic group? Considering that there are two primary alcoholic groups in the molecule of glycol, what different oxidation products can theoretically be obtained?

3. What is glycerol? How is glycerol obtained from the "spent lyes" of soap industry?

4. Give an account of the physical and chemical properties of glycerol.

5. How will you ascertain that the given solution contains glycerol?

6. Write down the full constitutional formulæ of Glycerol and Glycol.

7. How will you distinguish between solutions of glycerol and cane sugar?

CHAPTER XV.

OXALIC ACID AND TARTARIC ACID.

As there are alcohols containing more than one hydroxyl group, similarly there are acids which contain more than one carboxyl group. Those acids which contain two carboxyl groups are said to be dibasic. There are some acids which in addition to the carboxyl groups, contain some hydroxyl groups. They are known as **hydroxy acids.**

Names and Formulæ of some Hydroxy and Dibasic acids.

$$\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

Oxalic acid.

$$\begin{array}{l} \quad\;\; CO.OH \\ CH_2 \\ \quad\;\; \backslash CO.OH \end{array}$$

Malonic acid.

$$\begin{array}{l} CH_2.CO.OH \\ | \\ CH_2\ CO.OH \end{array}$$

Succinic acid.

$$\begin{array}{l} HO.CH.CO.OH \\ \quad\;\; | \\ \quad\;\; CH_2.CO.OH \end{array}$$

Monohydroxy succinic acid.
(Malic acid)

$$\begin{array}{l} HO.CH.CO.OH \\ \quad\;\; | \\ HO.CH.CO.OH \end{array}$$

Dihydroxy succinic acid.
(Tartaric acid)

$$\begin{array}{l} \quad CH_2.CO.OH \\ \quad | \\ HO.C.CO.OH \\ \quad | \\ \quad CH_2.COOH \end{array}$$

Citric acid.

$$\begin{array}{l} \quad OH \\ \;/ \\ C=O \\ \;\backslash \\ \quad OH \end{array}$$

Carbonic acid

$$\begin{array}{c} CH_3 \\ | \\ H-C-OH \\ | \\ CO.OH \end{array}$$

α hydroxy propionic acid.
(lactic acid.)

OXALIC ACID, $C_2H_2O_4$, $\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$

Oxalic acid occurs in many plants in the form of calcium or acid potassium salts. **Trifolia oxalis** *(Tipatya ghas, chukha ghas)* contains oxalic acid. When oxidised with nitric acid, many organic substances like cane sugar and glycerol, give oxalic acid.

Preparation 1. When sodium formate is heated to 250°C, sodium oxalate is produced.

$$2H.CO.ONa = \begin{array}{l} CO.ONa \\ | \\ CO.ONa \end{array} + H_2$$

2. Oxalic acid is manufactured by the oxidation of pine saw-dust with atmospheric oxygen in the presence of caustic alkalies. Any caustic alkali may be used but a mixture of the hydroxides of potassium and sodium has been found to give the best results.

Pine saw-dust is made into a paste with the caustic alkalies. This paste is heated on iron pans to about 250°C. with some stirring to allow air to come in contact with the whole of the material. A mixture of sodium and potassium oxalates is formed which is extracted with water. The extract is then boiled with lime, whereby calcium oxalate is precipitated and caustic soda and caustic potash are regenerated for being used with a fresh quantity of saw-dust.

$$\begin{array}{l}CO.ONa\\ |\\ CO.OK\end{array} + Ca\,(OH)_2 = \begin{array}{l}CO.O\\ |\\ CO.O\end{array}\!\!>Ca + NaOH + KOH.$$

The precipitated calcium oxalate is suspended in water and decomposed with *dilute* sulphuric acid. Oxalic acid goes in solution and calcium sulphate is precipitated out.

The solution is concentrated when oxalic acid crystallises out.

Properties. Oxalic acid is a colourless crystaline substance. It crystallises with two molecules of water of crystallization, ($C_2H_2O_4.2H_2O$). The water of crystallization can be removed by heating the crystals in a steam oven.

Oxalic acid is soluble in water and alcohol.

On careful heating oxalic acid gives formic acid and carbon dioxide.

$$\begin{array}{l}CO.OH\\ |\\ CO\;OH\end{array} = H.CO.OH + CO_2.$$

On strong ignition it gives carbon monoxide carbon dioxide and water.

$$\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} = CO + CO_2 + H_2O.$$

When oxalic acid is heated with conc. sulphuric acid, it loses the elements of water and evolves carbon monoxide and carbon dioxide.

Oxalic acid works as a weak reducing agent. It is easily oxidised to carbon dioxide and water by slightly warming it with acidified permanganate. The permanganate solution is decolourised.

$$2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 3H_2O + 5O.$$

$$C_2H_2O_4 + O = 2CO_2 + H_2O.$$

Experiment 27. Add a little dilute sulphuric acid to a solution of oxalic acid followed by potassium permanganate solution and warm. The colour will be discharged.

For this reason oxalic acid is used for the standardisation of permanganate solutions.

All oxalates are insoluble in water excepting those of sodium, potassium and ammonium. All oxalates are decomposed when they are heated with conc. sulphuric acid, evolving carbon monoxide and carbon dioxide.

Heated with glycerol, oxalic acid gives allyl alcohol or formic acid according to the conditions of the experiment.

Tests of oxalates. Soluble oxalates give a white precipitate of calcium exalate, when their solutions are treated with calcium chloride. This precipitate is insoluble in acetic acid but soluble in hydrochloric acid. (Distinction from tartrates and citrates).

Oxalates decolourise acidified solutions of permanganate.

TARTARIC ACID, *Dihydroxy succinic acid.*

$$\begin{array}{l} CH.\ (OH).CO.OH. \\ | \\ CH.\ (OH).CO.OH. \end{array}$$

Tartaric acid occurs in many fruits *e. g* , Tamarind (*Imli*). In the fermentation of grape juice, a quantity of "argol" (impure potassium hydrogen tartrate) is deposited. It is from this compound that commercial tartaric acid is obtained.

Argol is recrystallised and its acquous solution is boiled with calcium carbonate. Tartaric acid is converted partly into normal potassium tartrate which remains in solution, and partly into calcium tartrate which is precipitated out.

$$2C_4H_5O_6K + CaCO_3 = C_4H_4O_6Ca + C_4H_4O_6K_2 + CO_2 + H_2O.$$

It is filtered and the filtrate containing potassium tatrate is treated with calcium chloride which precipitates all the tartaric acid as calcium tartrate. The precipitate of calcium tartrate obtained from both the operations, is washed and treated with dilute sulphuric acid. Tartaric acid is liberated and goes into solution. This is filtered from insoluble calcium sulphate and is concentrated to crystallisation.

Tartaric acid forms large transparent crystals which are soluble in alcohol and water but insoluble in ether. It melts at about 170°C., but decomposes at this temperature.

Tartaric acid is dibasic and forms two series of salts.

When tartaric acid is reduced with hydrogen iodide (HI) it gives first malic and then succinic acid.

$$\begin{array}{l} \mathrm{CH.(OH).CO.OH.} \\ | \\ \mathrm{CH.(OH).CO.OH.} \end{array} + 2\mathrm{HI} = \begin{array}{l} \mathrm{CH.(OH).CO.OH.} \\ | \\ \mathrm{CH_2.CO.OH.} \end{array} + \mathrm{H_2O} + \mathrm{I_2}.$$

Malic acid.

$$\begin{array}{l} \mathrm{CH.(OH).CO.OH.} \\ | \\ \mathrm{CH_2.CO.OH} \end{array} + 2\mathrm{HI} = \begin{array}{l} \mathrm{CH_2.CO.OH.} \\ | \\ \mathrm{CH_2.CO.OH.} \end{array} + \mathrm{H_2O} + \mathrm{I_2}.$$

When heated with conc. hydrobromic acid, tartaric acid gives dibromo-succinic acid.

$$\begin{array}{l} \mathrm{CH.(OH).CO.OH.} \\ | \\ \mathrm{CH.(OH).CO.OH.} \end{array} + 2\mathrm{HBr} = \begin{array}{l} \mathrm{CHBr.COOH} \\ | \\ \mathrm{CHBr.COOH} \end{array} + 2\mathrm{H_2O}.$$

Tests of Tartaric Acid. Tartaric acid may be identified by the application of the following tests:

(1) When tartaric acid is heated alone, it chars giving out the smell of burnt sugar.

(2) It chars when it is heaten with conc. sulphuric acid.

(3) Tartaric acid or tartrates give a metallic mirror with ammoniacal silver nitrate.

Experiment 28. Warm a dilute solution of a tartrate with ammoniacal silver nitrate in a water bath. A mettallic mirror will be obtained.

(4) With calcium chloride tartaric acid or tartrates give a white precipitate of calcium tartrate, which is soluble in acetic acid or caustic alkalies (distinction from oxalates). The precipitate of calcium tartrate is generally obtained on shaking the mixture of the two solutions.

Tartaric acid may be distinguished from cane sugar by the application of the above tests and also by its acid reaction, and sour taste.

Tartrates. Normal potassium tartrate is soluble in cold water, while the acid salt is sparingly soluble. The acid salt is precipitated when excess of tartaric acid is added to a concentrated solution of neutral potassium salts (test for potassium). The acid salt is known as **cream of tartar.** Potassium sodium tartrate is known as **Rochelle salt.** Potassium antimonyl tartrate, $KC_4H_4O_6\ (SbO).\ \frac{1}{2}H_2O$, is known as **tartar emetic,** and is used as a mordant and also as an emetic.

EXERCISES ON CHAPTER XV.

1. How is oxalic acid obtained from pine sawdust ?

2. Write down the constitutional formula of tartaric acid. How does it occure in nature.

3. How can you distinguish an oxalate from a tartrate ?

4. What happens when :

(a) oxalic acid is heated alone,
(b) tartaric acid is heated alone,
(c) oxalic acid is heated with conc, sulphuric acid,
(d) oxalic acid is heated with glycerol ?

5. How does oxalic acid behave towards potassium permanganate ?

6. Name some of the more important salts of tartaric acid

7. What do you mean by the basicity of an acid ? What is the basicity of the following acids :—

Formic acid, Acetic acid, Oxalic acid, Sulphuric acid, Nitric acid, Phosphoric acid, and Tartaric acid ?

8. You are given a solution which may contain :

(a) cane sugar,

(b) Glycerol,

or (c) tartaric acid.

State how you would proceed to identify it.

9. How will you distinguish between sodium tartrate and sodium oxalate ?

CHAPTER XVI.

CARBOHYDRATES.

Carbohydrates are substances which contain carbon, hydrogen and oxygen the last two in the same proportion in which they are contained in water. These substances are of great importance from different points of view: chemical, industrial and physiological.

Classification.

Carbohydrates

(1) Monosaccharoses

(2) Disaccharoses $C_{12}H_{22}O_{11}$ *e.g.* cane sugar

(3) Trisaccharoses $C_{18}H_{32}O_{16}$

(4) Polysaccharoses $(C_6H_{10}O_5)n$ *e.g.* starch.

Monosaccharoses:

Aldoses *e.g.* Glucose

Ketoses *e.g.* Fructose

1. Monosaccharoses are polyhydroxy aldehydes or ketones containing from three to nine atoms of carbon. They are soluble, sweet substances and they do not crystallise well. Glucose (grape sugar) and Fructose (fruit sugar) are the typical examples of the class.

2. Disaccharoses may be regarded as obtained by the loss of one molecule of water from two molecules of hexoses (monosaccharoses containing six carbon atoms). On hydrolysis they give rise to hexoses. Most of them are soluble and crystallise well. They are sweet. Cane sugar (sucrose), maltose, and milk sugar (lactose) are some of the examples of the class.

3. Trisaccharoses may be regarded as substances produced by the loss of two molecules of water from three molecules of hexoses. On hydrolysis they give rise to hexoses.

4. Polysaccharoses are complex carbohydrates *e.g.*, starch, cellulose. They may be regarded as derived from a large number of molecules of hexoses by the loss of a certain number of molecules of water. They are insoluble in water, possess no sweet taste, and do not crystallise. On complete hydrolysis they give rise to hexoses.

Most of the naturally occuring carbohydrates are *optically active.*

GLUCOSE, *grape sugar*, or *dextrose*, $C_6H_{12}O_6$.

$$\begin{array}{l} CH_2—OH \\ \dot{C}H—OH \\ \dot{C}H—OH \\ \dot{C}H—OH \\ \dot{C}H—OH \\ \dot{O}HC \end{array}$$

The constitutional formula shows that glucose is an aldehyde and that it contains five hydroxyl groups in the molecule.

It occurs in many sweet fruits. **Glucosides** are the substances which occur in plants and are the combinations of glucose and certain other compounds. When they are hydrolysed, they form glucose and other substances. **Amygdalin** is a glucoside which occurs in bitter almonds, and gives glucose on hydrolysis. Glucose is prepared by the hydrolysis of complex carbohydrates like starch and cane sugar.

Glucose is a colourless substance which is soluble in water but insoluble in alcohol. It is sweet in taste.

It is not easily charred by conc. sulphuric acid.

Being an aldehyde it possesses strong reducing properties. It reduces ammoniacal silver nitrate and Fehling's solution. It reacts with phenyl hydrazine to give a hydrazone. Prussic acid gives a cyanhydrin.

It reacts with acetyl chloride to give a pentacetyl derivative. The formation of the pentacetyle derivative is a proof of the existence of five hydroxyl groups in the molecule of grape sugar. Phosphorus pentachloride gives a pentachloro derivative by the replacement of the five hydroxyl groupe by five chlorine atoms.

When it is oxidised, glucose gives first gluconic acid and then saccharic acid.

$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CO\text{—}OH \end{array}$$

Gluconic acid.

$$\begin{array}{l} CO\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CO\text{—}OH \end{array}$$

Saccharic acid.

With lime glucose forms a compound called calcium glucosate which is *soluble* in water.

It undergoes alcoholic fermentation with yeast.

FRUCTOSE, ***fruit sugar***, or ***laevulose***, $C_6H_{12}O_6$.

Fruit sugar occurs in many plants with glucose. It may be obtained from cane sugar by hydrolysis. When cane sugar is hydrolysed, an equimolecular mixture of glucose and fructose is obtained. When this mixture is boiled with milk of lime, calcium fructosate and calcium glucosate are produced. Calcium fructosate being less soluble, comes out of solution. It is separated, suspended in water and is decomposed by the action of carbon dioxide. Calcium carbonate is precipitated out and fructose goes into solution.

It is manufactured for the use of diabetic patients.

Fructose is a solid substance. It is soluble in water. Although it is a ketone, it shares many of the properties of glucose. It reduces Fehling' solution. It undergoes alcoholic fermentation with yeast, but less readily than glucose. It forms a pentacetyl and a pentachloro derivative with acetyl chloride and phosphorus pentachloride respectively showing thereby that it contains five hydroxyl groups in the molecule.

It reacts with phenyl hydrazine to form a phenyl hydrazone. The action of phenyl hydrazine is not limited to the simple formation of a hydrazone, in the case of both glucose and fructose. Some more complex reactions take place which are beyond the scope of this volume, to deal with.

SUCROSE, *can sugar* or *saccharose*, $C_{12}H_{22}O_{11}$.

Cane sugar occurs in many plants. Sugar cane and beet root are its chief commercial sources.

Manufacture of cane sugar. Cane sugar is generally manufactured from sugar cane and beet-root (Chaqundar).

1. *From sugar cane:* Sugar cane contains 15—20% sugar. The cane is passed between rollers so arranged that the maximum quantity of juice is extracted.

The juice so extracted contains vegetable protiens, some organic acids, andlsugar. The juice is boiled with

1 to 2% milk of lime which coagulates proteins and precipitates calcium salts of the organic acids. These rise to the surface forming a scum which is removed. Carbon dioxide is passed through the solution in order to decompose any calcium saccharate which might have been formed and to remove excess of lime as carbonate. The calcium carbonate so formed is filtered off and a dark coloured solution of sugar is obtained. It is decolourised by boiling with animal charcoal and filtered through linen bags.

Some times sulphur dioxide (SO_2) is used instead of carbon dioxide which yields a solution of much better colour. This process is known as *sulphitation* and avoids the use of animal charcoal.

The purified sugar solution is evaporated under reduced pressure to avoid charring. The solution is concentrated to the crystallization point. It is then run down in pans and cooled. The crystals are separated from the molasses by means of centrifugal machines.

3. **Sugar from Beet-root.** Beet-root contains sugar to the extent of 13 to 14% but improved varieties contain up to 17%.

The ripe roots are washed with water and cut into thin slices. The sugar is extrated by diffusion by passing hot water (80° to 90°), through a series of tanks containing slices. The extracted juice is treated in the same manner as in the case of sugar cane.

Cane sugar is a colourless crystalline substance, soluble in water but insoluble in strong alcohol. It melts at 160°C.

When it is heated strongly, it swells up giving out a characteristic odour. Ultimately it gives out all its hydrogen and oxygen leaving behind only carbon which is known as sugar charcoal.

Concentrated sulphuric acid behaves in a similar way. It extracts elements of water from sugar and converts it into carbon, which is deposited in the form of a black powder. Glucose is not charred by the action of sulphuric acid in the cold.

Experiment 29. Take solutions of cane sugar and grape sugar in two different test tubes. Add concentrated sulphuric acid to both the test tubes. The liquid will become dark in the test tube in which cane sugar was taken while in the case of grape sugar, the solution will not undergo any charge in colour.

Cane sugar does not react with phenyl hydrazine.

When cane sugar is oxidised with conc. nitric acid, it gives oxalic acid. When a solution of cane sugar is warmed with dilute mineral acids, it is hydrolysed to a mixture of grape sugar and fruit sugar. The mixture is known by the name of **invert sugar.** Cane sugar does not reduce Fehling's solution; but when it has been hydrolysed it reduces Fehling's solution.

Experiment 30. Take a small quantity of cane sugar. Dissolve it in water and divide the solution into two parts. To one part add Fehling's solution and boil. No reddish yellow precipitate will be produced.

To the other portion add a few drops of hydrochloric acid and warm. Now add Fehling's solution and boil. A reddish yellow precipitate of cuprous oxide is produced.

Repeat the experiment with a dilute solution of grape sugar. Fehling's solution will be reduced directly by the solution.

STARCH, $(C_6H_{10}O_5)n$.

Starch occurs in plants as reserve food material in various forms of granules having *organised* structure. It is insoluble in cold water. On boiling with water, it forms a paste.

When boiled with dilute sulphuric acid, starch is first hydrolysed to **dextrin,** which gives a red colouration with iodine while starch is turned blue. Long boiling with dilute sulphuric acid, converts starch into glucose, which gives no colouration with iodine.

The blue colour produced by the action of iodine on starch is a characteristic test for starch. An unstable compound is produced, which is decomposed on boiling. Starch is a useful substance of great commercial importance. It is largely used for the manufacture of glucose and also in laundries.

Production of glucose from starch. Take a thin paste of starch in hot water in a beaker and add a few drops of dilute sulphuric acid and boil. The starch is first converted into dextrine which gives red colour with iodine. Ultimately it is hydrolysed to glucose which gives no colour with iodine. It is one of the methods for the manufacture of glucose.

Comparison of Glucose, Cane sugar and Starch.

Properties.	Glucose.	Cane sugar.	Starch
State.	Solid, amorphous.	Solid crystalline.	Solid amorphous.
Formula.	$C_6H_{12}O_6$.	$C_{12}H_{22}O_{11}$.	$(C_6H_{10}O_5)_n$.
Solubility in water.	Soluble.	Soluble.	Insoluble.
Action of con. sulphuric acid.	Does not char in the cold.	Chars easily.	Chars.
Boiling with Dil. H_2SO_4.	No effect.	Hydrolysed to invert sugar.	Hydrolysed first to dextrin and finally to glucose.
Iodine solution.	No effect.	No effect.	Blue colour.
Fehling solution.	Reduces.	No reduction without hydrolysis	No reduction.

CELLULOSE, $(C_6H_{10}O_5)n$.

Cellulose is the chief constituent of plant cell walls. Cotton, linen, and filter paper are the purest forms of cellulose.

In comparison to the other carbohydrates, cellulose is very inactive. Chlorine, bromine and dilute mineral acids have no action on cellulose.

Strong caustic alkalies have a dissolving effect on cellulose. This property is made use of in **mercerising** cotton. When cotton fibres are soaked in a strong solution of caustic soda, for some time, the outer portion of the walls of the fibres becomes thickened and when it is washed, and dried, it acquires a silky appearance.

Paper dipped in strong sulphuric acid, becomes tough and transparent. It is known as **parchment paper.**

When boiled with hydrochloric or sulphuric acid, cellulose is hydrolysed into glucose.

Concentrated nitric acid, specially in the presence of sulphuric acid gives various nitrates which are of great technical importance. **Gun cotton** is cellulose hexa-nitrate. It is highly explosive.

Celluloid (xylonite) consists of the lower nitrates of cellulose. It is soluble in acetone. With camphor it is largely used in industry, for the manufacture of various articles like combs, toys, films etc.

EXERCISES ON CHAPTER XVI.

1. What are carbohydrates? How are they classified?

2. Give an account of the occurrence and properties of glucose.

3. How will you distinguish between glucose and cane sugar both supplied in the form of their aqueous solutions?

4. What are the chief sources of sucrose? In what respects does it differ from glucose?

5. How does starch occur in nature? What happens when starch is boiled with dilute sulphuric acid?

6 What is invert sugar? How can you obtain a sample of glucose from cane sugar?

7. How do cane sugar, grape sugar, and fruit sugar behave towards yeast?

8. What is Fehling's solution? How does it behave towards glucose and sucrose?

9. You are supplied with three test tubes containing starch paste, and solutions of grape sugar and cane sugar respectively. How will you identify them?

10. How will you distinguish between the solutions of glucose and acetaldehyde?

11. How would you demonstrate the production of glucose from cane sugar and starch respectively?

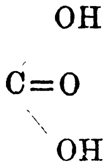
12. There are three carbohydrates in your course: starch, cane sugar and glucose. Show how they resemble and differ.

13. What simple tests would you carry out to show that (i) "Gur" (from sugar cane juice) contains both cane sugar and grape sugar; (ii) wheat contains starch; (iii) tincture of iodine contains alcohol?

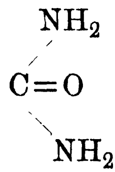
CHAPTER XVII.

UREA.

Urea is the amide of carbonic acid (H_2CO_3). It is also known a **carbamide.**



Carbonic acid.



Urea (carbamide).

Urea occurs in urine of *mammals*, birds and *reptiles*, in large quantities. A grown up man excretes about 30 grams of urea every day. It is regarded as the final oxidation product of nitrogenous compounds in the body.

It was the accidental formation of urea from ammonium cyanate (NH_4CNO) which showed that organic compounds could be synthesised in the laboratory.

Preparation. 1. Urea may be obtained from urine by (*a*) evaporating and treating with nitric acid whereby urea nitrate separates out which is decomposed with barium carbonate; or (*b*) by concentrating and extracting with alcohol, which dissolves urea. The alcoholic solution is evaporated when urea is left as residue.

2. When ethyl carbonate is heated with ammonia, urea is produced.

$$\begin{array}{l} \quad O\,C_2H_5 \\ \;\,/ \\ C{=}O \\ \;\,\backslash \\ \quad O.C_2H_5 \end{array} + 2NH_3 = \begin{array}{l} \quad NH_2 \\ \;\,/ \\ C{=}O \\ \;\,\backslash \\ \quad NH_2 \end{array} + 2C_2H_5.OH.$$

This reaction is analogous to the formation of acetamide from ethyl acetate and ammonia.

3. Urea is obtained by heating ammonium cyanate.

$$N.C.O.NH_4 = H_2N.CO.NH_2$$

An **intramolecular change** (rearrangement of atoms in the molecule) takes place, whereby ammonium cyanate is converted into urea without any loss or gain of material.

Instead of using ammonium cyanate, usually a mixture of potassium cyanate and ammonium sulphate is employed.

4. When carbonyl chloride ($COCl_2$, phosgene) gas is treated with ammonia, urea is produced.

$$\begin{array}{l} \quad Cl \\ \;\,/ \\ C{=}O \\ \;\,\backslash \\ \quad Cl \end{array} + 2NH_3 = \begin{array}{l} \quad NH_2 \\ \;\,/ \\ C{=}O \\ \;\,\backslash \\ \quad NH_2 \end{array} + 2HCl.$$

(Compare with the action of ammonia on acetyl chloride).

Properties. Urea is a white crystalline solid substance. It possesses a cooling taste and is soluble in water and alcohol but insoluble in ether. It melts at 132°C.

Heated slowly, it evolves ammonia, and forms biuret.

$$NH_2.CO\ NH\boxed{H + NH_2.}CONH_2 = NH_2.CO.NH.CO.NH_2 + NH_3$$

If urea is heated strongly, the biuret which is produced decomposes with the evolution of more of ammonia.

Experiment 31. Take a small quantity of urea in a dry test tube. Heat the test tube carefully so that it continues to evolve ammonia Cool the test tube and dissolve the contents in a small quantity of water. Add a drop of very dilute copper sulphate solution followed by excess of caustic soda solution. A violet colour will be produced If the heating is carried too far, biuret will decompose and the test will fail. The test fails also if a large amount of copper sulphate is present.

As an amide urea is hydrolysed by heating with acids and alkalies.

$$CO:(NH_2)_2 + H_2O = CO_2 + 2NH_3.$$

Treated with nitrous acid, urea gives carbon dioxide, nitrogen and water.

$$CO:(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

Nitrogen is also evolved by the action of sodium hypochlorite or hypobromite.

$$CO:(NH_2)_2 + 3NaBrO = CO_2 + 2H_2O + 3NaBr + N_2.$$

Experiment 32. Take a dilute solution of urea in a test tube and add a solution of sodium hypobromite (bromine dissolved in solution of caustic soda). A brisk reaction will take place and nitrogen will be evolved.

The behaviour of nitrous acid and hypochlorite or hypobromite is utilized for the estimation of urea in urine. The evolved nitrogen is collected over caustic potash which absorbs carbon dioxide. The volume of nitrogen is read and the corresponding amount of urea is calculated. It should be noted that when nitrous acid is used, only half of the nitrogen comes from urea, while in the case of hypochlorite or hypobromite, all the nitrogen evolved is obtained from urea.

When an aqueous solution of urea is treated with excess of nitric acid, a crystalline white precipitate of urea nitrate is obtained which is insoluble only in the presence of nitric acid. Urea nitrate is $CO:(NH_2)_2.HNO_3$ and not $CO:(NH_2).(HNO_3)_2$. as might be expected.

EXERCISES ON CHAPTER XVII.

1. How will you obtain a sample of urea from urine ?

2. Describe the physical and chemical properties of urea.

3. How will you estimate the quantity of urea in a given sample of urine ?

4. What is the molecular formula of urea nitrate ? How will you obtain urea nitrate from urine and urea ?

5. What is the action of sodium hypobromite and nitrous acid on urea ? Give equations.

6. How can urea be prepared in the laboratory from substances which are regarded to be inorganic ?

7. How will you ascertain that the given solution contains urea ?

8 Compare urea with acetamide.

9. How will you distinguish between urea and acetamide ?

10. You are given the following white solid substances : cane sugar, oxalic acid, starch, and urea. Mention the tests by which you would identify each substance.

CHAPTER XVIII.

AROMATIC COMPOUNDS.

The term aromatic is originally derived from "aroma" which means an agreeable odour. It included some compounds which were found to possess an agreeable odour and also some peculiarities in their properties. But as the knowledge of organic chemistry advanced, it was found that there are some compounds belonging to this class which possess a very offensive odour. The term is still in use but the original meaning is no longer applicable. Now it simply means a class of compounds belonging to the **benzene series**. As methane is the parent substance of all the compounds belonging to aliphatic series, similarly benzene is the parent substance of all the aromatic compound.

The main source of aromatic compounds which is obtained as a bye product in the destructive distillation of coal in the manufacture of coal gas or coke. It is a dark coloured thick liquid of specific gravity 1·1 to 1·2. It is a mixture of a large number of organic compounds. Formerly it was considered to be a waste product and most of it was thrown away. It is now a source of a large number of highly important substances such as dyes and medicines etc.

Coal tar Distillation. The tar is subjected to fractional distillation in iron retorts and stills. The vapours are condensed and the distillate is usually collected into the following four factions :

Temperature.	Fraction.	Constituents.
1. 80°—170°C	Light oil	Benzene and its homologues.
2. 170°—230°	Middle oil or carbolic oil	Carbolic acid, naphthalene.
3. 230°—270°	Heavyoil or Creosote oil	Phenol, creosote aniline, Pyridine.
4. 270°—400°	Anthracene oil	Anthracene.
5. Residue in retort is pitch which is used on roads.		

The light oil is the most important of all the products of the distillation. It is allowed to stand when the crude fraction separates into two layers. The upper layer is the oily liquid and the lower one is the ammoniacal liquor which is drawn off. In addition to benzene and its homologues it contains basic substances *e. g.*, pyridine and acidic substances *e. g.*, phenol. It is agitated with caustic soda to remove the acid impurities and with dilute sulphuric

acid to get rid of the basic impurities. It is then washed with water. The neutral oil thus obtained is fractionally distilled and the first fraction distilling upto 95° C. is separated and contains about 90% of benzene (benzol).

BENZENE. Benzene is a product of coal tar distillation. It may be synthetically produced by passing acetylene through a red hot tube.

As methane can be obtained by heating sodium acetate with soda lime, similarly benzene may be obtained by heating sodium benzoate with soda lime.

$$CH_3 \ \boxed{CO\ ONa + NaO} H = CH_4 + Na_2CO_3.$$

$$C_6H_5. \ \boxed{CO\ ONa + NaO} H = C_6H_6 + Na_2CO_3.$$

Experiment 33. Take a small quantity of sodium benzoate in a dry test tube and add to it dry soda lime, and heat. Smell of benzene will be observed and benzene can be lighted at the mouth of the test tube where it will burn with a smoky flame.

Properties. Benzene is a colourless, mobile liquid. It boils at 80° C. It possesses a characteristic odour and burns with a luminous smoky flame.

Experiment 34. Take a few drops of benzene in a watch glass, and apply flame. Observe the luminosity of the flame. Bring a cold porcelain basin over the flame and observe the amount of carbon deposited on the basin.

Benzene is lighter than water and is also immiscible with it. It is a good solvent for many substances which do not dissolve in water, *e. g.* resins, fats, phosphorous, and iodine.

Unlike methane and other aliphatic hydrocarbons, benzene reacts with nitric acid and sulphuric acid, to form nitrobenzene and benzene sulphonic acid respectively.

$$C_6H_6 + HNO_3 = C_6H_5.NO_2 + H_2O.$$
$$C_6H_6 + H_2SO_4 = C_6H_5.HSO_3 + H_2O.$$

Formation of such compounds by the action of nitric and sulphuric acids, is the characteristic property of the aromatic compounds.

When benzene is reduced under suitable conditions, it forms hexahydro-benzene by the addition of six atoms of hydrogen.

$$C_6H_6 + 6H = C_6H_{12}.$$

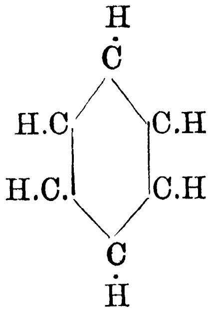
In this respect it resembles ethylene and acetylene (unsaturated hydrocarbons).

Treated with chlorine or bromine, in the presence of sunlight, benzene gives addition products ($C_6H_6Cl_6$,$C_6H_6Br_6$) again showing resemblance with the unsaturated hydrocarbons.

Chlorine and bromine in the presence of a carrier (Fe or I_2) work as substituents giving mono-, di-, tri-, etc. chloro or bromo benzene. In this respect it resembles methane (saturated hydrocarbons).

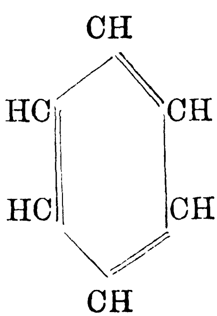
Iodine has no direct action at ordinary temperatures but in the presence of certain substances which can destroy the hydrogen iodide produced, substitution products are obtained.

The molecule of benzene is represented by a hexagon, there being one carbon atom at each corner.

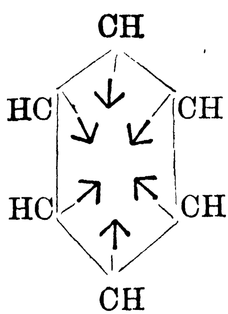


From the above formula it is clear that the fourth valency of any of the six carbon atoms has not been represented. There is a controversy about this fourth valency. Sometimes it is represented by putting double bonds alternately between two carbon atoms, as in (1) below, and sometimes the fourth valency is directed towards the centre, as in (2).

It has become a common practice to represent the benzene molecule simply by means of a hexagon.



(1)

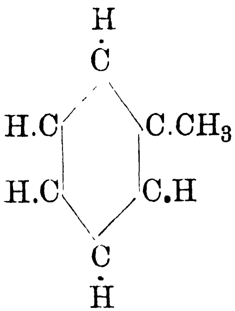


(2)

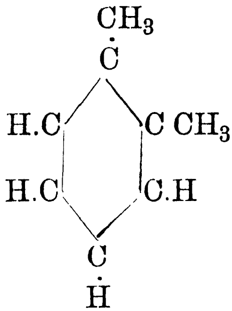
The Phenyl Group. As the molecule of a saturated hydrocarbon, minus an atom of hydrogen, is known an alkyl group, similarly a molecule of benzene less an atom of hydrogen, is called a **phenyl group.**

C_2H_6	$-C_2H_6$	$C_2H_5\,Cl.$
Ethane.	Ethyl group.	Ethyl chloride.
C_6H_6	$-C_6H_5$	$C_6H_5.Cl.$
Benzene.	Phenyl group.	Phenyl chloride.

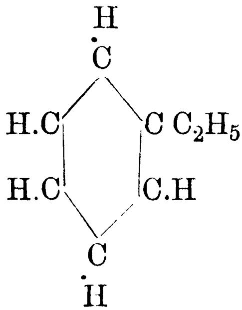
Homologues of Benzene. The formulae of the homologues of benzene are obtained by the replacement of one or more atoms of hydrogen of the benzene molecule by alkyl groups.



Toluene.
(Methyl benzene)



Xylene.
(Dimethyl benzene)

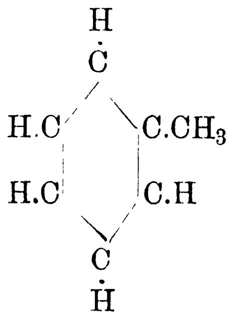


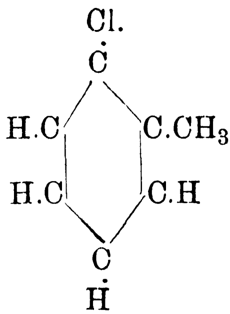
Ethyl benzene.

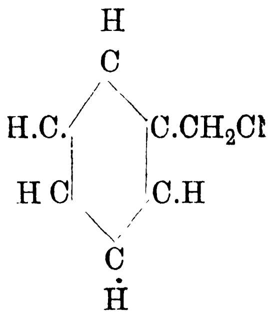
Homologues of benzene form two distinct classes of substitution products :—

1. Those in which the substituting radical enters the **nucleus,** *i. e.* by the replacement of an atom of hydrogen attached to a carbon atom which forms part of the benzene ring.

2. Those in which the substituting radical enters the **side chain**, (that part of the molecule which is out of the nucleus), by the replacement of an atom of hydrogen attached to a carbon atom which does not form a part of the ring.







Toluene — Monochloro-toluene (Nucleus substitution) — Benzyle chloride (Side chain substitution)

Derivatives obtained by substitution in the side chain possess almost all the properties of aliphatic compounds.

NITROBENZENE, $C_6H_5NO_2$.

It has already been mentioned that benzene, when treated with nitric acid, gives nitrobenzene. Better results are obtained when conc. sulphuric acid is also present.

Experiment 35. Mix together 80 c. c. of concentrated nitric and 30 c.c. of conc. sulphuric acid and cool. Add this mixture very slowly to 25 c.c. of benzene contained in a round bottomed flask. The temperature of the mixture should not be allowed to go beyond 60°C. If it goes higher, the flask should be cooled by immersing it in cold water. When all the acid has been added, heat the flask in water bath for about half an hour. The contents of the flask are

cooled and added to water. Nitrobenzene being heavier forms the lower layer which is separated and purified by washing with water and with sodium carbonate and finally with water. It is dried with calcium chloride.

Nitrobenzene is a liquid which boils at 205°C. It possesses an odour which resembles that of the oil of bitter almonds. It is immiscible with water. Commercially it is known as **oil of mirbane.** It is sometimes used for adultrating oil of bitter almonds. Its chief use is in the manufacture of aniline.

ANILINE, $C_6H_5.NH_2$.

When nitrobenzene is reduced with acid reducing agents, aniline is produced. On the commercial scale, iron filings and hydrochloric acid are used as the reducing agents. When the reduction is complete, the mixture is subjected to steam distillation. In the distillate aniline settles as the lower layer which is drawn off. It is dehydrated with solid caustic potash and purified by redistillation.

Aniline is an oily liquid which boils at 184°C. It possesses a characteristic odour and is sparingly soluble in water, but soluble in alcohol and hydrochloric acid. It is basic in nature. It forms salts with acids which are soluble in water.

$$C_6H_5.NH_2 + HCl = C_6H_5NH_2.HCl$$

Aniline hydrocloride.

$$2C_6H_5NH_2 + H_2SO_4 = (C_6H_5.NH_2)_2H_2SO_4.$$

Aniline sulphate.

Like methyl and ethyl amines, aniline gives the isocyanide reaction with chloroform and caustic soda.

$$C_6H_5\,NH_2 + CHCl_3 + 3KOH = C_6H_5NC + 3KCl + 3H_2O.$$

When treated with nitrous acid, aniline gives phenol ($C_6H_5.OH$) at ordinary temperatures. This shows that the reaction is similar to the action of nitrous acid on the aliphatic amines. But in the case of aniline an intermediate product of great synthetic value can be obtained, if the reaction is conducted at low temperatures (below 10°C). Such products are known as **diazonium salts.** No such products are obtained when the aliphatic amines are treated with nitrous acid.

$$C_6H_5.NH_2 + HNO_2 = \underset{\text{(at ordinary temps).}}{C_6H_5.OH} + N_2 + 2H_2O.$$

$$C_6H_5.NH_2 + HCl + HNO_2 = \underset{\substack{\text{Diazobenzene chloride} \\ \text{(at low tempts.)}}}{C_6H_5N:NCl} + 2H_2O.$$

Tests of aniline. 1. It gives the carbamine reaction with chloroform and caustic alkalies.

2. With potassium dichromate and concentrated sulphuric acid, it gives first a red, then blue and finally a black colour.

3. When aniline is treated with bromine water, a slightly pink precipitate of tribrom-aniline is produced.

Uses of aniline. Aniline is a substance of great commercial importance and is largely used in the

manufacture of synthetic dyes. In the laboratory it is used for the preparation of benzene derivatives.

Comparison with Aliphatic amines. Aniline resembles ethyl and methyl amines in the following properties :

1. Basic character (formation of salts with acids) :

2. Action of nitrous acid to form hydroxy derivatives at ordinary temperatures :

3. Giving isocyanide reaction with chloroform and potash.

It differs from the aliphatic primary amines in being less basic and in giving the diazo compounds.

The true representatives of aliphatic amines in the aromatic series are the compounds in which the amino group is present in a side chain *e. g.* $C_6H_5\,CH_2.NH_2$, benzyl amine.

PHENOL, *carbolic acid,* C_6H_5OH.

Phenol is a derivative of benzene containing one hydroxyl group in the nucleus of the benzene molecule.

It has already been mentioned that when aniline is treated with nitrous acid, and the mixture is warmed, phenol is produced. It may be obtained from benzene by passing through the following changes :

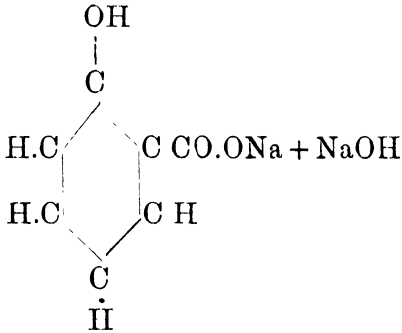
$$C_6H_6 \xrightarrow{HNO_3} C_6H_5.NO_2 \xrightarrow{H} C_6H_5.NH_2 \xrightarrow{HNO_2} C_6H_5.OH.$$

Phenol may also be obtained by fusing benzene, sulphonic acid with caustic potash.

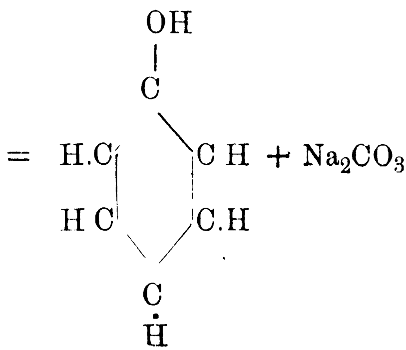
$$C_6H_6 + H_2SO_4 = C_6H_5.SO_3.H + H_2O.$$

$$C_6H_6SO_3H + 2KOH = C_6H_5.OH + K_2SO_3 + H_2O.$$

When salicylic acid or sodium salicylate is heated with sodalime, phenol is produced.



Sodium salicylate



Phenol.

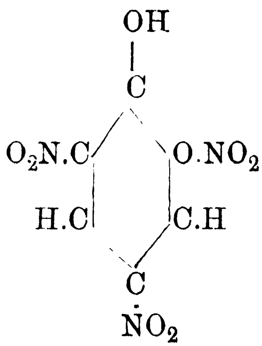
Phenol is manufactured from the middle oil of coaltar distillation. It is a colourless, crystalline deliquescent solid which melts at 42°C. On exposure it turns pink. It boils at 183°C. It possesses a characteristic odour. It is poisonous, corrosive and

sparingly soluble in water. It behaves like a weak acid. It possesses strong antiseptic properties.

Phenol gives a violet colouration with ferric chloride. It gives a slightly pinkish precipitate with bromine water. It dissolves in caustic soda forming sodium phenate, $C_6H_5.ONa$.

With phosphorous pentachloride, phenol gives the chloride, ($C_6H_5.Cl$, mono-chloro-benzene).

When phenol is treated with conc. nitric acid in the presence of sulphuric acid, it gives **picric acid**, a trinitro-phenol.



Picric acid.

Picric acid is used in medicine and surgery as an antiseptic and also as an explosive. It dyes silk and wool yellow.

When phenol is treated with a small quantity of sodium nitrite, followed by conc. sulphuric acid, a dark green colour is obtained which changes to pink on dilution with water. **(Liebermann's Reaction).**

Experiment 36. In a dry test tube take a small quantity of phenol. Add to it a very small crystal of sodium nitrate. The crystal of the nitrate should not be bigger than the size of a pin's head. Shake the test tube, and add conc. sulphuric acid and shake again. A dark green colour will be produced. Dilute the contents of the test tube with water, the colour will change to pink.

Comparison with Alcohol. Phenol resembles ethyl alcohol in the following properties :—

1. The hydrogen of the hydroxyl group is replaced by sodium by treatment with sodium ;

$$2C_2H_5.OH + 2Na = 2C_2H_5.ONa + H_2.$$

$$2C_6H_5.OH + 2Na = 2C_6H_5.ONa + H_2.$$

2. The hydroxyl group is replaced by chlorine on treatment with phosphorous pentachloride.

$$C_2H_5.OH + PCl_5 = C_2H_5.Cl + POCl_3 + HCl.$$

$$C_6H_5\ OH + PCl_3 = C_6H_5.Cl + POCl_3 + HCl.$$

3. Ethers are produced by treatment with alkyl halides.

$$C_2H_5.OH + C_2H_5.I = C_2H_5-O-C_2H_5 + HI.$$

$$C_6H_5.OH + C_2H_5I = C_6H_5.O.C_2H_5 + HI.$$

Phenyl methyl ether.

Phenol differs from ethyl alcohol in the following points :

1. Phenol is acidic while alcohol is neutral. Phenol reacts with caustic alkalies while alcohol does not react with alkalies.

2. Phenol can be nitrated and sulphonated while alcohol can neither be sulphonated nor nitrated.

3. Phenol gives a colouration with ferric chloride while alcohol does not react with this reagent.

4. Phenol does not form esters with acids so readily as ethyl alcohol.

5. Phenol does not give aldehydes and acids on oxidation.

The true representatives of aliphatic alcohols in the benzene series, are the compounds which contain the hydroxyl group in the side chain, (*e. g.* benzyl alcohol, $C_6H_5CH_2.OH$).

Uses of phenol. Being a strong germicide, it is used in surgery. It is also used for the preparation of certain dyes, explosives and medicines.

BENZYL ALCOHOL, $C_6H_5.CH_2.OH$.

Benzyl alcohol is a true aromatic alcohol.

It may be obtained by any of the following methods :—

1. By treatment of benzyl chloride with caustic potash :

$$C_6H_5.CH_2.Cl + KOH = C_6H_5.CH_2.OH + KCl.$$

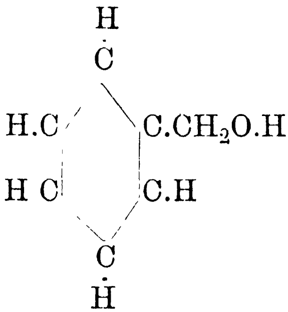
2. By the action of caustic potash on benzaldehyde.

$$2C_6H_5.CHO + KOH = C_6H_5\,CH_2\,OH + C_6H_5.CO.OK.$$

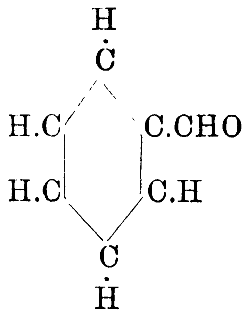
3. By the reduction of benzamide.

$$C_6H_5.CONH_2 + 4H = C_6H_5.CH_2.OH + NH_3.$$

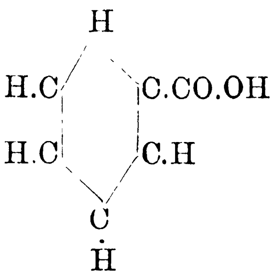
Benzyl alcohol is a colourless liquid which boils at 24°C. It possesses all the properties of aliphatic alcohols. When it is oxidised it gives first benzaldehyde and then benzoic acid. It reacts with acids to form esters.



Benzyl alcohol.



Benzaldehyde.



Benzoic acid.

BENZALDEHYDE, $C_6H_5.CHO$.

Benzaldehyde is the aldehyde of benzoic acid. It may be obtained by any of the following methods :—

1. Oxidation of benzyl alcohol.

$$C_6H_5.CH_2OH + O = C_6H_5.CHO + H_2O.$$

2. Dry distillation of calcium benzonate with calcium formate.

$$(C_6H_5.CO.O)_2Ca + (H.COO)_2Ca = 2C_6H_5.CHO + 2CaCO_3.$$

The above two methods are analogous to the methods of preparation of acetaldehyde.

3. From amygdalin which is a glucoside containing prussic acid and benzaldehyde. On hydrolysis amygdalin gives benzaldehyde, prussic acid and glucoso.

Properties. Benzaldehyde is a colourless liquid which boils at 179°C. It is immiscible with water and is heavier. It is miscible with alcohol and ether. It possesses the characteristic odour of the oil of bitter almonds.

Benzaldehyde resembles acetaldehyde and the other aliphatic aldehydes in the following properties :—

1. On oxidation gives benzoic acid.

2. On reduction gives benzyl alcohol.

3. Reduces ammonical silver nitrate.

4. Reacts with hydrocyanic acid, hydroxyl amine and phenyl hydrazine.

5. Gives benzal chloride ($C_6H_5CHCl_2$) with phosphorous pentachloride.

The following are the main points of difference between benzaldehyde and acetaldehyde :—

1. Benzaldehyde does not reduce Fehling's solution ;

2. It does not polymerise ;

3. With ammonia benzaldehyde gives a crystalline compound but of quite a different nature ;

4. With caustic alkalies benzaldehyde does not form resinous products. A reaction takes place in which one molecule is oxidised at the expense of the other. There is a simultaneous oxidation and reduction.

$$2C_6H_5.CHO + KOH = \underset{\text{Benzyl alcohol}}{C_6H_5\,CH_2.OH} + \underset{\text{Potassium Benzoate.}}{C_6H_5.COOK}$$

BENZOIC ACID, $C_6H_5\,COOH$.

Benzoic acid may be obtained by the oxidation of benzyl chloride, benzyl alcohol, toluene, or benzaldehyde.

$$C_6H_5CH_2.Cl + 2O = C_6H_5.COOH + HCl$$
$$C_6H_5.CH_2OH + 2O = C_6H_5.COOH + H_2O$$
$$C_6H_5.CH_3 + 3O = C_6H_5.COOH + H_2O$$
$$C_6H_5.CHO + O = C_6H_5.COOH$$

Benzoic acid is manufactured by the oxidation of benzyl chloride with nitric acid.

It occurs in **gum benzoin** (*Loban*) and may be obtained by subliming the gum.

Benzoic acid is a crystalline white solid. It melts at 121°C. It sublimes readily. It is insoluble in cold water, but is soluble in hot water, ether and alcohol. Indian grocers call it *Korıa loban ka sat* (कौड़िया लोबान का सत).

Most of the metallic salts of benzoic acid are soluble.

With phosphorus pentachloride, benzoic acid gives benzoyl chloride ($C_6H_5.CO.Cl$) which when treated with ammonia gives benzamide (C_6H_5 $CO.NH_2$).

Benzoic acid is a monobasic acid and forms salts and esters.

Benzoic acid and benzoates may be identified by the following tests :—

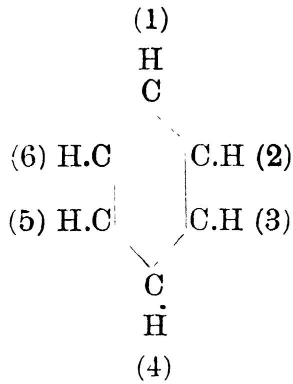
1. Treated with ferric chloride, solutions of benzoates give a buff coloured precipitate.

2. When heated with soda lime in a dry test tube, benzoates evolve benzene which may be identified by its peculiar odour and also by its combustion at the mouth of the test tube, where it will burn with a smoky flame.

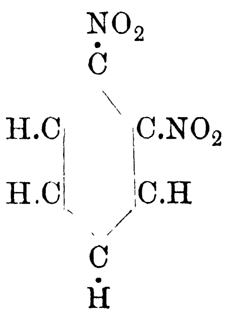
Benzoic acid clcsely resemble acetic acid and other fatty acids with regard to its methods of preparation and properties.

Di-substitution Products of Benzene. A di-substitution product of benzene occurs in three isomeric forms, ortho–,meta–, and para-. If the six carbon

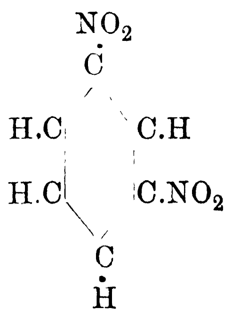
atoms of the benzene nucleus are consecutively numbered, 1, 2, 3, 4, 5, and 6, and if the substituting groups or elements enter the positions 1 and 2, or 1 and 6, the compound produced is called the ortho-compound. The compound produced by substitution in positions 1 and 3, or 1 and 5, is called a meta-compound, while that which is produced by substitution in position 1 and 4, is known as the para-compound.



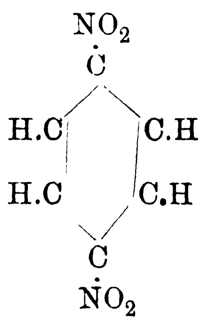
Benzene.



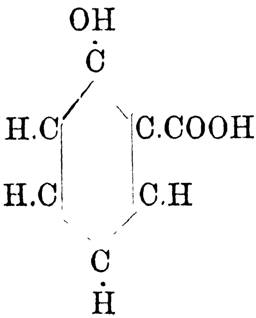
Ortho dinitro benzene



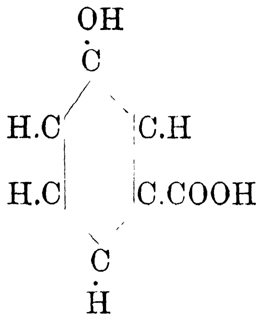
metadinitro benzene



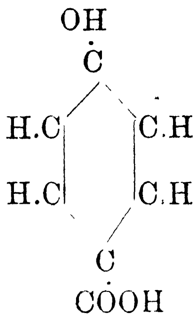
Paradinitro benzene



Ortho hydroxy benzoic acid (salicylic acid)



Metahydroxy benzoic acid



Parahydroxy benzoic acid

SALICYLIC ACID, C_6H_4 (OH) COOH.

Salicylic acid is the **orthohydroxy benzoic acid.** It occurs in the oil of wintergreen in the form of its methyl ester methyl salicylate.

$$C_6H_4(OH)COOCH_3.$$

Salicylic acid is a crystalline white solid, which melts at 155°C. It is sparingly soluble in cold but freely soluble in hot water. With ferric chloride it gives an intense violet colouration.

When salicylic acid is heated with soda lime in a dry test tube, it gives out phenol.

Owing to the antiseptic properties of salicylic acid, it is used in medicine and surgery.

EXERCISES ON CHAPTER XVIII.

1. What do you understand from the expression "Aromatic Compounds"? How does bezene differ from paraffins?

2. What is the action of nitric acid and sulphuric acid on benzene and ethane respectively?

3. What is the action of nitrous acid on aniline? Compare aniline with methyl amine.

4. What is phenol? How does it differ from ethyl alcohol? What substances in aromatic series are analogous to ethyl alcohol?

5. How will you show that the given solution contains ammonium benzoate?

6. What happens when,

(*a*) Benzoic acid is heated with soda lime,

(*b*) Salicylic acid is heated with soda lime,

(*c*) Ferric chloride is added to phenol,

(*d*) Ferric chloride is added to a solution of a benzoate;

(*e*) Benzoic acid is treated with phosphorus pentachloride?

CHAPTER XIX.

Amino acids and Proteins.

The formula of an amino acid is obtained by replacing one atom of hydrogen from the alkyl group of an acid, by $-NH_2$ group

$CH_3\,COOH$	$NH_2CH_2-COOH.$
Acetic acid	Amino acetic acid (glycine)

Amino acetic acid is the parent substance of this class. It is also known as **glycine** or **glycocol.**

Glycine may be prepared by the action of ammonia on cloracetic acid.

$$Cl-CH_2-COOH+NH_3 = NH_2-CH_2-COOH+HCl$$

Ultimately ammonia will give ammonium salt of the acid and ammonium chloride.

$$Cl-CH_2-COOH+3NH_3 = NH_2-CH_2-COONH_4 + NH_4Cl$$

It may also be prepared by the hydrolysis of gelatin or glue by boiling with dilute mineral acids or alkalies.

The acid crystallizes in colourless prisms. When heated it chars before it melts; consequently no definite melting point is assigned to it. It has a sweet taste and is soluble in water but insoluble in ether or alcohol.

The presence of the carboxyl group imparts acidic properties while that of the $-NH_2$ group basic properties to the substance. It is acidic as well

as basic. It, therefore, forms salts with bases and also with acids.

$$NH_2-CH_2-COOH+NaOH=NH_2-CH_2-COONa+H_2O$$

$$NH_2-CH_2-COOH+HCl=\underset{\text{glycine hydrochloride}}{HClNH_2-CH_2-COOH.}$$

Copper aminoacetate $(NH_2CH_2-COO)_2\ Cu-H_2O$ is the most characteristic salt of the acid.

As an acid it forms esters and amides.

$$\underset{\text{Ethyl aminoacetate}}{NH_2-CH_2-COOC_2H_5}$$

$$\underset{\text{Aminoacetamide.}}{NH_2-CH_2-CONH_2}$$

As in the amines, nitrous acid replaces the amino group by a hydroxyl group with evolution of nitrogen.

$$NH_2-CH_2-COOH+HNO_2 = \underset{\text{Hydroxy acetic acid}}{HO-CH_2-COOH}+N_2+H_2O$$

Formulae of some other amino acids.

$$\underset{\displaystyle NH_2}{CH_3-\overset{}{CH}-COOH} \qquad \alpha\text{—amino propionic acid (alanine)}$$

$$(CH_3)_2\ CH-CH_2-\underset{\displaystyle |\atop NH_2}{CH}-COOH \qquad \alpha\text{—amino isobutyl acetic (leucine)}$$

Importance of Amino acids.

The importance of the amino acids lies in the fact that they are regarded to be the units for the formation of proteins which are the predominating

nitrogenous substances of the plant and animal tissues. On hydrolysis, proteins give rise to amino acids.

PROTEINS.

As already mentioned proteins are the main nitrogenous constituents of animal and plant bodies. They are regarded to have been built up of long chains of molecules of amino acids by the loss of molecules of water. In addition to carbon, hydrogen nitrogen, and oxygen, proteins also contain phosphorus and sulphur.

Protein *metabolism* is regarded to be a sign of life in animals.

Like carbohydrates and fats, they are important food materials for animals Plants manufacture their own proteins, but animals are incapable to do so. Ultimately they depend upon plants for the supply of proteins.

Protein content (percentage) of some common food materials.

	Proteins	Carbohydate	Fat
Meat	16·6	×	29·8
Eggs	12·3	×	11 3
Bread (डबलरोटी)	7·0	48·3	0·7
Fish	15·7	×	0·1
Milk	3·3	4 8	3·6
Orange	0·8	8 8	83·4
Butter	0·6	0·1	
Potato	1·5	19·9	0·02

Though exact determinations of the molecular weights of proteins have not been made, it is certain that they have very high molecular weights as is evident from the low values of osmotic pressure exhibited by solutions of proteins.

Reactions and Tests of Proteins.

1. When treated with **concentrated nitric acid** solutions of proteins give a white precipitate

2. Xanthoproteic Reaction :—Protein solutions give a white precipitate with concentrated nitric acid. When this precipitate is boiled it turns yellow. If it is cooled and ammonia is added the precipitate turns orange.

3. Milon's reagent:—This reagent contains mercurous and mercuric nitrates with some pure nitric acid in solution in water. When this reagent is added to a protein solution a white precipitate is obtained which turns brick red on boiling.

4. Adamkiewicz' Reaction :—Excess of glacial acetic acid or a solution of glyoxalic acid is added to the protein solution and concentrated sulphuric acid is poured down the side of the test tube. A violet ring is formed at the junction of the two liquids.

5. Rosenheims Formaldehyde Reaction :—A very dilute solution of formaldehyde is added to the protein solution. Concentrated sulphuric acid containing a trace of some oxidising agent *e. g.* ferric chloride or hydrogen peroxide, is added by the side of the test tube. A purple coloured ring is formed.

6. Rose's Test :—One drop of a very dilute solution of copper sulphate is added to the protein solution followed by caustic potash. A violet colour develops.

APPENDIX A.

Some peculiarities of Organic Compounds

1. All organic compounds contain carbon.

2. Isomerism is of very general occurrence in carbon compounds, while it is very rare in the compounds of other elements Na_2SO_4 represents only one compound, sodium sulphate, while C_2H_6O represents ethyl alcohol and dimethyl ether which are absolutely different substances

3. In carbon compounds the chemical changes are generally very slow, while they are very quick in the case of inorganic compounds Caustic soda and sulphuric acid react almost instantaneously to form sodium sulphate and water, but the action between ethyl alcohol and acetic acid to form ethyl acetate and water is never complete.

4. The carbon atoms have got the peculiarity of combining with one another in large numbers to form long chains. It is due to this property that the carbon compounds are so complex, and their number is so large.

APPENDIX B.

Aromatic and Aliphatic Compounds

*AROMATIC	ALIPHATIC
1. All are closed chain compounds ;	1. Mostly they are open chain compounds :
2. The parent substance of the series is Benzene :	2. The parent substance of the series is Methane ;
3. Concentrated Nitric acid gives Nitro compounds ; $C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$. (The process is known as Nitration.)	3. Nitric acid has generally no action on the hydrocarbons ; the nitro derivatives are obtained by the action of silver nitrite on the halogen derivatives of the paraffins ;
4. Concentrated Sulphuric acid gives sulphonic acids : $C_6H_6 + H_2SO_4 = C_6H_5SO_3H + H_2O$ (The process is known as sulphonation.)	4. Sulphuric acid has no action on the hydrocarbons : the sulphonic acids are prepared indirectly ;
5. The halogen derivatives (*e. g.*, Chlorobenzene) are not very reactive : the halogen atom cannot be exchanged for other radicals :	5. The halogen derivatives are very active : the halogen atoms can be exchanged for other radicals :

*The true Aromatic substitution products are those which contain the substituting radical in the nucleus.

AROMATIC	ALIPHATIC
6. The hydroxy derivatives (Phenols) are acidic in nature ;	6. The hydroxy derivatives (Alcohols) are neutral in nature ;
7. The amino derivatives (*e.g.*, Aniline) are less basic and can be diazotized.	7. The amino derivatives (amines) are strongly basic and cannot be diazotized.
8. Aldehydes :	8. Aldehydes :
(a) Do not reduce Fehling's solutions ;	*(a)* Reduce Fehling's solution ;
(b) Do not form brown resinous products with caustic alkolies ;	*(b)* Form resinous products with caustic alkalies ;
(c) Do not form aldehyde-ammonia with ammonia ;	*(c)* Form aldehyde-ammonia ;
(d) Do not polymerise ;	*(d)* Polymerise ;
(e) Do not give cyanhydrins with potassium cyanide.	*(e)* Form cyanhydrins with potassium cyanide.

APPENDIX C.

Detection of the Elements present in Organic Compounds.

Carbon is the essential constituent of all the Organic Compounds. Of the other elements Hydrogen and Oxygen are the most common. Nitrogen, Halogens, Sulphur and Phosphorus come next and the remaining elements are generally rare.

CARBON.

The organic substance if solid is heated with copper oxide or if the substance is gaseous or liquid the vapours are passed over heated copper oxide. Carbon dioxide is evolved in each case which may be identified by passing it through lime-water which will turn milky.

$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$$

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$$

HYDROGEN.

In testing for hydrogen, the compound is similarly heated with copper oxide. If hydrogen is present in the compound, water will be produced which will condense in the form of small drops on the cooler parts of the apparatus.

NITROGEN.

(1) **Conversion of Nitrogen into Cyanide:** The substance is heated with metallic sodium in a dry test tube till it completely chars. The hot test tube is broken in a small quantity of water contained in a basin. The contents of the basin are stirred and filtered. If nitrogen is present in the compound, sodium cyanide is formed which goes in solution together with a relatively large quantity of caustic soda.

It now remains to test for the presence of cyanide. The solution is warmed with ferrous sulphate, whereby ferrocyanide is preduced. If the solution is now acidified with hydrochloric acid and a few drops of ferric chlorides solution are added, a prussian blue precipitate should be obtained. The intensity of the colour of the precipitate or solution depends upon the quantity of sodium cyanide produced.

$$2NaCN + FeSO_4 = Fe(CN)_2 + Na_2SO_4$$

$$4NaCN + Fe(CN)_2 = \underset{\text{sodium ferrocyanide}}{Na_4Fe(CN)_6}$$

$$3Na_4Fe(CN)_6 + 4FeCl_3 = \underset{\text{ferric ferrocyanide}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

Experiment 37.—Take a small quantity of the substance (*e. g.*, acetamide) in a dry test-tube. Add to it a small piece of freshly cut and dried metallic sodium, and heat cautiously to avoid the rapid oxidation of sodium and voltilisation of the organic compound. When the first action is over, heat strongly till the base of the test tube becomes red hot. Break the test tube in a small quantity of water contained in a porcelain basin. Filter and to a portion of the

filtrate add a few drops of a strong solution of ferrous sulphate. Warm and acidify with hydrochloric acid Add a drop or two of ferric chloride solution A blue or green precipitate or colour indicates the presence of Nitrogen

If the original substance is gaseous the gas may be passed over hot sodium. In the case of a liquid substance, the best results are obtained by adding a drop ar two of the liquid to melted sodium.

(2) **Conversion of Nitrogen into Ammonia :** When some organic compounds containing nitrogen are strongly heated with soda-lime, ammonia is evolved which turns red litmus into blue.

SULPHUR.

The organic compound is heated with sodium in the same way as in the case of nitrogen. Sodium sulphide is formed which gives a violet colouration with a solution of sodium nitroprusside.

HALOGENS.

(1) **Flame test :** A clean copper wire is strongly heated in a bunsen flame till it ceases to givo any green colouration and is coated with a film of the black oxide of copper. The wire is now touched with the organic compound and is brought into the flame again. If it imparts a bluish green colouration to the flame, a halogen is present in the compound. The cupric oxide combines with the halogen of the compound and forms cupric halide, which is volatile in the flame and imparts the characteristic colouration.

(2) **Conversion of the Halogen into the Sodium halide :** When the compound is heated with metallic sodium, the halogen is converted into the sodium halide, which may be identified by adding silver nitrate. Before adding this reagent the excess of caustic soda which is invariably present must be neutralised with nitric acid.

If nitrogen is present in the organic compound, sodium cyanide is formed which gives a white precipitate with silver nitrate in presence of nitric acid. But if the solution is evaporated to a small bulk after adding nitric acid, the cyanide is decomposed.

The individual halogens may be tested for by heating the silver salt with concentrated sulphuric acid and manganese di-oxide.

OTHER SUBSTANCES.

Phosphorus is converted into phosphoric acid by oxidation under proper conditions, which is identified in an ordinary way.

Sometimes metals also are present in organic compounds. The presence of the metals can be detected by strongly heating the organic substance on a nickel foil. If a residue is left on the foil, a metal is present.

The nature of the metal can be determined by examining the residue in the ordinary way.

APPENDIX D.

Estimation of Elements Present in an Organic Compound.

CARBON AND HYDROGEN.

The estimation of carbon and hydrogen is effected by burning a known quantity of the substance in a slow current of *dry* and *carbon dioxide free* air or oxygen in presence of cupric oxide, in weighed *calcium chloride tubes* and *potash bulbs* respectively.

The combustion is carried on in a hard glass tube heated with a series of gas burners.

The copper oxide which is put at the further end of the tube between asbestos plugs, is heated in a current of pure dry air to remove any carbon dioxide and moisture from the tube and the copper oxide. A small weighed quantity of the substance, in a small glass bulb if liquid or in a porcelain boat if solid, is now introduced. Most of it will be burnt into carbod dioxide and water, while if some of it is volatilised unburnt, it will be oxidised by copper oxide. The calcium chloride tubes absorb moisture and the carbon dioxide is taken up by the potash bulbs. The current of air is continued for some time even after oxidation to remove the last traces

of the moisture and carbon dioxide from the combustion tube to the absorbing apparatus.

The increase in the weight of the calcium chloride tubes gives the weight of water while that in the weight of the potash bulbs gives the weight of carbon dioxide produced. From these weights the percentage of carbon and hydrogen in the compound can easily be calculated.

Example:—2·39 gms. of an organic compound on combustion in excess of oxygen gave 0·88 gram of carbon dioxide and 0·18 gram of water. Calculate the percentage of hydrogen and carbon in the compound.

44 Parts by weight of CO_2 contain 12 parts by weight of carbon.

$\therefore$ 0·88 grams contain $\frac{12 \times 0{\cdot}88}{44}$ grm. carbon

Now 2·39 grms. of the compound contain

$\frac{12 \times 0{\cdot}88}{44}$ grm. of carbon

$\therefore$ 100 grm. contain $\frac{12 \times 0{\cdot}88 \times 100}{44 \times 2{\cdot}39}$ grms. of carbon

which is equal to 10·04%.

18 Parts by weight of water contain 2 parts by weight of hydrogen

$\therefore$ 0·18 grm. contain $\frac{2 \times 0{\cdot}18}{18}$ grm. hydrogen

Now 2·39 grms. of the compound contain

$$\frac{2 \times 0{\cdot}18}{18} \text{grm. of hydrogen}$$

$\therefore$ 100 grms. contain $\dfrac{2 \times 0{\cdot}18 \times 100}{18 \times 2{\cdot}39}$ hydrogen

which comes to 0·836%.

OXYGEN.

There is no direct method for the estimation or identification of oxygen. The organic compound is analysed qualitatively and also quantitative. If the percentage of the different elements *together* is short of one hundred it is believed that the deficiency is due to the presence of oxygen. The difference is regarded to be the percentage of oxygen in the compound

NITROGEN.

(1) **Evolution of Nitrogen in the free state :—** (*Duma*) The compound (known weight) is heated with copper oxide in a hard glass tube from which air has already been expelled by passing a current of carbon dioxide. The nitrogen of the compound is evolved in the free state and is collected over caustic potash. When the action is complete a current of carbon dioxide is again passed to sweep away any nitrogen which is present in the tube. The volume, temperature and pressure of the gas are measured and its weight is calculated.

(2) **Conversion of Nitrogen into Ammonia** *(Will and Varrentrapp)*: A known weight of the substance is heated with freshly heated soda-lime, the nitrògen is converted into ammonia and is absorbed in a **known** volume of **standard** sulphuric acid. After the reaction is complete the excess of sulphuric acid is determined by titrating it with standard alkali. The quantity of ammonia corresponding to the quantity of sulphuric acid consumed is calculated from which the quantity of nitrogen is easily obtained.

(3) **Conversion of the Nitrogen into Ammonium sulphate by heating with concentrated sulphuric acid:** *(Kjeldahl)*: A known weight of the substance is boiled with concentrated sulphuric acid with the addition of a little potassium permanganate. The nitrogen is converted into ammonium sulphate. The liquid is made strongly alkaline with caustic soda and the ammonia is boiled off which is absorbed in a known volume of standard hydrochloric or sulphuric acid. The excess of the acid is determined by titration with standard alkali from which the quantity of nitrogen is calculated as in (2).

Examples:—(1) 0·1186 grm. of Acetamide was heated with copper oxide in a hard glass tube in the usual way. The volume of Nitrogen evolved was 25 c. c., measured at 22°C. and 740 mm, pressure. Calculate the percentage of Nitrogen in the compound.

25 c. c. of Nitrogen at 22°C. and 740 mm. will occupy $\frac{25 \times 740 \times 273}{760 \times 295}$ c. c. at N. T. P., which comes to 22·52 c. c. or 0·02252 litre.

22·4 litres of Nitrogen at N. T. P. weigh 28 grams. (gram molecule)

$\therefore$ 0·02252 ,, ,, ,, ,, $\frac{28 \times 0·02252}{22·4}$ grm.

=0·02814 grm.

0·1186 grm. of acetamide contains 0·02814 grm. of nitrogen.

$\therefore$ 100 grms. ,, ,, $\frac{100 \times 0·02814}{0·1186}$ grm. of nitrogen.

Which comes to 23·72%.

(2) 0·354 grm. of acetamide was heated with soda lime, the ammonia was dissolved in 100 c. c of N/10 sulphuric acid. After the reaction was complete, the excess of acid was titrated with N/10 standard alkali, of which 40 c. c. were required for neutralization. Calculate the percentage of nitrogen in acetamide.

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4$$

According to the above equation :

98 grms. of H_2SO_4 require 34 grms. of ammonia.

or 49 ,, ,, ,, 17 ,, ,,

or 4·9 ,, ,, ,, 1·7 ,, ,,

or 1,000 c.c. of N/10 H_2SO_4
require 1·7 ,, ,,

In the above reaction 40 c.c. of N/10 alkali were required to neutralise the excess of acid, which comes to 40 c c. of N/10 acid. This shows that out of 100 c.c. of the acid, 40 c c. remained unacted upon and $100-40=60$ c.c. were neutralised by ammonia.

1,000 c.c. of N/10 acid correspond with 1.7 grms. of ammonia.

60 c.c. ,, ,, $\frac{1 \cdot 7 \times 60}{1000}$ grm.

Which is equal to 0·102 grm. of ammonia.

But 17 grms. of ammonia contain 14 grms. of nitrogen.

$\therefore$ 0·102 grm. of ammonia contains $\frac{14 \times 0 \cdot 102}{17}$ $=0 \cdot 084$ grm. of nitrogen.

Now 0·354 grm. of acetamide contains 0·084 grm. of nitrogen,

100 grms. ,, ,, $\frac{100 \times 0 \cdot 084}{0 \cdot 354}$ grms.

which comes to 23·72%.

HALOGENS.—A known weight of the compound is heated with fuming nitric acid under pressure, and in presence of silver nitrate. The halogen is precipitated in the form of the silver halide, which is separated by filtration, and is washed, dried and weighed. The weight of the halogen is calculated from the weight of the silver halide.

The heating is conducted in a thick walled sealed tube of hard glass which is heated in a specially constructed furnace (the sealed tube furnace) for several hours. The temperature of the furnace is kept at about 200° or above according to the nature of the substance.

Example :—0·5516 grm. of chloral hydrate when heated with fuming nitric acid and silver nitrate, gave 1·435 grms. of silver chloride. Calculate the the percentage of chlorine in chloral hydrate.

143·5 grms. AgCl contain 35·5 grms. of Chlorine

1·435 " " " $\frac{35\cdot5 \times 1\cdot435}{143\cdot5}$ " "

which comes to 0·355 grm.

0 5516 grm. of chloral hydrate contains 0·355 grm. of chlorine

100 grms. " " " $\frac{0\cdot355 \times 100}{0\cdot5516}$ " "

which is equal to 64·4%.

SULPHUR.—When organic compounds containing sulphur are heated with fuming nitric acid and barium chloride in a sealed tube, the sulphur is converted into barium sulphate, which may be washed, dried and weighed. The weight of sulphur is then calculated from the weight of barium sulphate.

The organic compound containing sulphur may also be oxidised with potassium nitrate in presence of caustic potash and alcohol. The sulphur is con-

verted into potassium sulphate. When the oxidation is complete, the whole mass is extracted with water and filtered from carbonaceous matter. It is then treated with an excess of barium chloride. The precipitated $BaSO_4$ is filtered, washed, dried, and weighed as usual.

Example:—0·19 grm of Thio-urea when oxidised and treated with barium chloride gave 0·5825 grm. of barium sulphate What is the percentage of sulphur in thio-urea ?

233 grms. of $BaSO_4$ contain 32 grms. of Sulphur.

0·5825 ,, ,, ,, $\dfrac{32 \times 0{\cdot}5825}{233}$,, ,,

$= 0{\cdot}08$ grm.

Now 0·19 grm. of Thio-urea contains 0·08 grm. of sulphur.

100 ,, ,, ,, $\dfrac{100 \times 0{\cdot}08}{0{\cdot}19}$,, ,,

which comes to 42·105%,

APPENDIX E.

Determination of the Molecular weight of an organic compound

The following are some of the more important methods for the determination of the molecular weight of an organic compound :—

1. Vapour Density Method ;
2. Rising of Boiling Point Method ;
3. Lowering of Freezing point Method ;
4. Special Method for Organic bases.

Vapour Density Method.

$$\text{Vapour Density} = \frac{\text{Mass of a certain volume of gas or vapour}}{\text{Mass of the same volume of hydrogen at the same temperature and pressure.}}$$

But equal volumes of different gases at the same temperature and pressure, contain equal number of molecules. (*Avogadro's Hypothesis*). Therefore the above equation may be written as :

$$\text{V. D.} = \frac{\text{Mass of } N \text{ molecules of the gas or vapour}}{\text{Mass of } N \text{ molecule of hydrogen.}}$$

$$= \frac{\text{Mass of one molecule of gas or vapour}}{\text{Mass of one molecule of hydrogen}}$$

But the mass of one molecule of hydrogen is 2.

$$\text{V. D.} = \frac{\text{Mass of one molecule of gas or vapour}}{2}$$

But the mass of one molecule of the gas or vapour is the molecular weight of the gas or vapour in the same units in which 2 has been taken to be the mass of hydrogen molecule and may be represented by M.

$$\text{V. D.} = \frac{M}{2}$$

or $M=2d$, where d represents the vapour density.

There are various methods for the practical determination of the vapour density of organic liquids, but the following two are of general application :

(a) Victor Meyer's Method ;
and *(b)* Duma's Method.

(a) **Victor Meyer's Method** :—The determination of vapour density of an organic liquid by this method is conducted in a special apparatus which is called the Victor Meyer's vapour density apparatus. It consists of a long tube *A* which has an elongated bulb at the closed end. It is provided with a delivery tube which opens under water contained in a glass trough. The open end of the tube *A* is closed with an ordinary cork. The tube *A* is surrounded with a glass jacket *B*. The apparatus is fitted as shown in the figure. The liquid of which the vapour density is to be determined is taken in a small weighed bottle

(Hoffman's bottle) and is weighed. The difference gives the weight of the liquid taken.

Before starting, a small plug of asbestos wool is put at the bottom of the tube *A* to guard against the fracture of the glass when the bottle is dropped. The bulb of the jacket is half filled with a liquid of which the boiling point is higher than that of the liquid of which the vapour density is to be determined. This liquid is boiled and is continued in this state

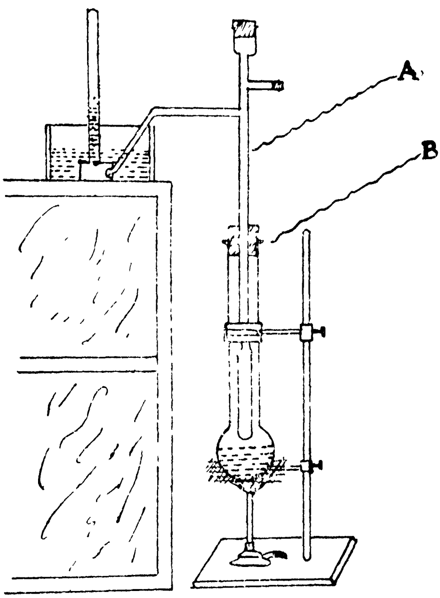


Figure 17.

throughout the experiment. The air contained in the tube *A* expands and escapes through the opening

of the delivery tube. When air ceases to come out of this opening, a graduated tube, filled with water is inverted over the mouth of the delivery tube The cork is removed for a while and the pottle is dropped. The cork is replaced immediately after the bottle has been dropped.

The liquid in the bottle expands and its stopper is thrown off. The vapours of the liquid displace an equal volume of air which is collected in the graduated tube. When air bubbles have ceased to come out, the apparatus is disconnected and the graduated tube is transferred to a long cylinder containing water. It is pushed down into the cylinder till the level of water outside and inside the graduated tube is the same. The temperature of the water contained in the cylinder is noted and the barometer and the volume of the air contained in the graduated tube are read.

The calculation of the vapour density will be clear from the following example.

Example.—In a Victor Meyer determination, 0·0926 grm. of a liquid displaced 28·19 c c. of air, collected over water and measured at 16°C. and 753·6 mm. Calculate the vapour density and molecular weight of the liquid.

The observed pressure is the combined pressure of the air and also the water vapour contained in the

graduated tube. Therefore the pressure exerted by air is the observed pressure minus the tension of water vapour at 16°C. (Dalton's law of partial pressures)

which comes to $753{\cdot}6 - 13{\cdot}6 = 740{\cdot}00$ mm.

$$d = \frac{\text{Mass of a certain volume of gas or vapour}}{\text{Mass of the same volume of hydrogen at the same T and P.}}$$

The mass of the vapour is the same as the mass of the liquid $= 0{\cdot}0926$ grm. We have to find out the mass of 28·9 c c. of hydrogen at 16°C. and 740 mm. which at N. T. P. will occupy

$$\frac{28{\cdot}9 \times 273 \times 740}{(16+273) \times 760} = 26{\cdot}58 \text{ c.c.}$$

One c c. of hydrogen at N.T.P. weighs 0·00008987 grm. The weight of 26·58 c c. of hydrogen at N.T.P. $= 0{\cdot}002388\ldots$ grm. Substituting these values in the above equation,

$$d = \frac{0\ 0926}{0\ 002388} = 38{\cdot}77$$

The molecular weight $= 2 \times 38{\cdot}77 = 77{\cdot}54$

Alternative Method.

The weight of 26·58 c.c. of the vapours at N. T. P. $= 0{\cdot}0926$ grm.

The weight of 22·4 litres of the vapours at N.T.P.

$$= \frac{0\ 0926 \times 22{\cdot}4 \times 1{,}000}{26\ 58} = 78{\cdot}04 \text{ grms.}$$

This is the gram molecule of the substance.

Therefore the molecular weight of the substance is 78·04.

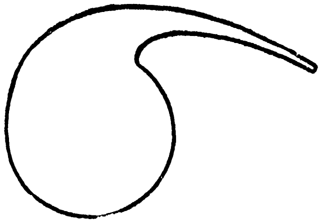


Figure 18.

(b) **Duma's Method:**—A glass bulb as shown in the figure is taken and is warmed by rubbing between the hands. When still warm the small opening of the bulb is immersed in the liquid of which the vapour density is to be determined. Some of the liquid will be sucked into the bulb. By repeating this operation, about three cubic centimeters of the liquid are sucked in. The bulb is now placed into a hot bath the temperature of which is higher than the boiling point of the liquid. The liquid boils and the vapours escape through the small opening till the temperature of the contents of the bulb is equal to the temperature of the bath which is noted. When the vapours have ceased to come out, the end of the bulb is sealed in a blow pipe flame. The bulb is thoroughly dried and weighed again.

The end of the bulb is now broken under water. Owing to the reduced pressure inside the bulb,

water will rush in and will completely fill the bulb. The bulb is again weighed.

It will be observed that there have been three weighings in the whole operation.

1. wt. of glass of the bulb and air.
2. wt. of glass of the bulb and vapour
3 wt. of glass of the bulb and water.

The calculation will be clear from an example.

Example.—A Duma's bulb full of air weighed 27 26 grams at 12°C and 740 mm. Full of vapour at 99°C. and the same pressure it weighed 27·69 grms. The same bulb full of water weighed 239·86 grams. Find the vapour density of the substance.

1. Weight of glass of bulb + air =27·26 grms.
2. Weight of glass of bulb + vapour = 27·69 grms.
3. Weight of glass of bulb + water =239·86grm.

If from (3) we subtract (1) we will get the weight of water which is contained in the bulb. (The weight of air is negligible in comparison to the weight of water).

∴ The weight of water = 239·86—27·26 = 212·6 grms. The weight of water in grams may be taken as the volume of water in c.c.

∴ The capacity of the bulb = 212·6 c c

Now it is required to calculate the weight of

212·6 c.c. of air measured at 12°C. and 740 mm. pressure, which at N. T. P. will occupy,

$$\frac{212{\cdot}6 \times 740 \times 273}{760 \times 285} = 198{\cdot}2 \text{ c. c.}$$

1,000 c.c. of air at N.T.P. weigh 1·293 grm.

∴ 198·2 c.c. of air at N.T.P. weigh

$$\frac{1{\cdot}293 \times 198{\cdot}2}{1{,}000}$$

$$= 0{\cdot}25627 \ldots\ldots\ldots \text{grm.}$$

By subtracting this weight of air from (1), the weight of the glass of the bulb will be obtained.

27·26 − 0·256 = 27·004 grms. (wt. of glass)
Subtracting this from (2),

27 69 − 27·004 = 0·686 grm. (wt. of vapour)

All the above calculations show that 198·2 c. c. of the vapours measured at N.T.P. weigh 0·686 grm.

The weight of 22·4 litres of the vapour will be,

$$\frac{0{\cdot}686 \times 22{,}4 \times 1\,000}{198{\cdot}2} = 77{\cdot}5 \text{ grms.}$$

This being the gram molecule of the vapour, represents the molecular weight of the substance.

Therefore the molecular weight of the substance is 77·5.

The Boiling Point Method:—Gram molecules of difference substances (which do not ionise in solution)

when dissolved in the same weight of the same solvent raise the boiling point of the liquid to the same degree. If this constant say for one hundred grams of the solvent is determined by using solutes of known molecular weights, the molecular weight of an unknown substance can be determined by conducting the experiment with known weights of the solvent and the solute, and substituting the values in the following equation.

$$M = \frac{100 \times K \times w}{d \times W}$$

Where M is the molecular weight, K the constant for 100 grams, w the weight of the solute, d the rise in the boiling point, and W the weight of the solvent.

The following are the constants for 100 grams of some of the common solvents :—

Water	5·2
Alcohol	11·5
Acetone	16·7
Ether	21·1
Acetic acid	25·3
Benzene	26·7
Aniline	32·2
Chloroform	36 6

Example :—A solution of 0·674 gram of Camphor in 6·81 grms. of acetone gave an elevation of 1·09° in the boiling point. Calculate the molecular weight of Camphor in acetone.

$$M = \frac{100 \times K \times w}{d \times W} = \frac{100 \times 16\cdot7 \times 0\cdot674}{1\cdot09 \times 6\cdot81} = 151\cdot6$$

The results may be calculated even without the application of the formula.

For an elevation of 1·09° in 6·81 grms. (acetone) the quantity $= 0\cdot674$ grm.

For an elevation of 1·09° in 100 grms. (acetone) the quantity $= \frac{0\cdot674 \times 100}{6\cdot81}$ grms.

For an elevation of 16·7° in 100 grms. (acetone) the quantity $\frac{0\cdot674 \times 100 \times 16\cdot7}{1\cdot09 \times 6\cdot81} = 151\cdot6$ grms.

This must be the gram molecule of the substance and represents the molecular weight.

The Freezing Point Method :—Gram molecules of different substance (which do not dissociate in solution) when dissolved in the same weight of the same solvent lower the freezing point of the liquid to the same degree. The calculations etc. are obviously the same as in the case of the Boiling Point Method.

The following are the constants for 100 grms. of some of the common solvents :—

Water	18·8
Acetic acid	39·0
Benzene	50·0
Phenol	75·0

Example:—A solution of 0·147 grm. of Napthalene in 20·25 grms. of Benzene showed a depression of 0·284°. Calculate the Molecular weight of Naptha-lene.

$$M=\frac{100 \times K \times w}{d \times W}=\frac{100 \times 50 \times 0·147}{0·284 \times 20·25}=127·6$$

Special Method for Organic Acids :—The acid is converted into its silver salt by treating the ammonium salt of the acid with silver nitrate. The silver salts of organic acids are generally insoluble or only sparingly soluble. The salt is washed and dried, and a known quantity is taken in a weighed crucible and heated strongly to remove all the organic matter. The crucible is weighed again and the weight of the residue (silver) is obtained by difference. The ***basicity*** of the acid being known, the molecular weight of tho acid is calculated.

Example :—0·5 grm. of a silver salt of a monobasic acid gave 0·2358 grm. of silver. Calculate the molecular weight of the acid.

As the acid is monobasic, the gram molecule of the silver salt contains only 108 grams of silver.

0·2358 grm. of silver is contained in 0·5 grm. of the silver salt.

108·0 grm of silver is contained in $\frac{108 \times 0·5}{0·2358}$ grm. of the silver salt.

Which comes to 229 008.

$\therefore$ 229·008 represents the molecular weight of the silver salt. The molecular weight of the acid is obtained from this by subtracting 108 (atomic weigh) of silver) and adding 1 (atomic weight of hydrogent.

$$\text{Molecular weight of the acid} = 229{\cdot}008 - 108{\cdot}0 + 1$$
$$= 122{\cdot}008.$$

Special Method for Organic Bases:—Like ammonia the organic bases form crystalline chloroplatinates of the general formula $B_6H_2PtCl_2$, where B represents the formula of the *monacid* base. The base is dissolved in a slight excess of hydrochloric acid and platinic chloride added. The precipitated chloroplatinate is carefully washed and dried. A portion of this salt is weighed and ignited in a crucible and weighed again. The residue in the crucible is metallic platinum. The molecular weight of the base is calculated from the above observations, as will be clear from the following example.

Example:—A mono-acid organic base was converted into its chloroplatinate 0 80 grm. of which gave 0 25 grm. of platinum. Calculate the molecular weight of the base.

One gram molecule of the chloroplatinate contains 195 grams. of platinum.

0·25 grm. of platinum is contained in 0·8 grm. of platinum salt.

195·0 grm. of platinum is contained in $\frac{0{\cdot}8+195}{0{\cdot}25}$ grm. of platinum salt = 624 grms.

This represents the molecular weight of the chloro-platinate of which the formula is $B_2H_2PtCl_6$. If from this, molecular weight corresponding to H_2PtCl_6 is deducted and the result is halved, the molecular weight of the base is obtained.

$$H_2PtCl_6 = 410$$

$$\therefore \text{ The molecular weight of base} = \frac{624-410}{2}$$

$$= 107.$$

APPENDIX F.

Separation of the Constituents of a mixture.

So far as physical state is concerned, matter exists in three different forms.

1. Solid,
2. Liquid,

and 3. Gaseous.

A binary mixture (a mixture composed of two substances) may contain,

1. two solids,
2. a solid and a liquid,
3. a solid and a gas,
4. two liquids,
5. a liquid and a gas,

or 6. two gases.

These may be considered one by one in the order given above.

1. **Separation of a solid from another solid.**—When both the components of a mixture are solid substances they may be separated by one of the following methods.

(*a*) **Solubility**, One of the components of a mixture may be extracted with a suitable solvent in which the other component is insoluble. The simplest

example is a mixture of sand and sugar. When this mixture is shaken with water, the sugar goes into solution while sand remains undissolved which can be removed by filtration. Similarly sulphur can be separated from powdered iron by the solvent action of carbon-disulphide.

(*b*) **Fractional crystallization.** When both the constituents are soluble in a solvent and there is sufficient difference in their solubilities, they may be separated by fractional crystallization. The solution is concentrated till it is saturated with respect to the less soluble substance which partly crystallizes out together with a small quantity of the more soluble substance. By repeating this process with the mother liquor and the crystals, sufficient quantities of almost pure constituents can be obtained. The method is laborious and wasteful, but in certain cases it has proved very useful and proved the only method for the separation of the constituents.

(*c*) **Magnetic and Electrical effects.** The constituents of certain mixtures may be separated by magnetic and electrical effects. Iron may be separated from sulphur by stirring the mixture with a magnet.

If a mixture of red lead (Pb_3O_4) and flowers of sulphur is thrown in a thin layer over an ebonite plate which has been rubbed with flannel the particles of red lead which become positively charged adhere to the negatively charged plate. If the plate

is now tapped gently on a piece of paper, all the sulphur together with a small quantity of red lead falls off.

(d) **Sublimation.** Sometimes one of the constituents of a mixture is more volatile and can be separated by sublimation. Iodine, sulphur, ammonium chloride and various other substances can be separated from non-volatile substances by this method.

(e) **Chemical method.** When none of the above methods in which the chemical nature of the substance has not been changed, is applicable, a chemical method may be resorted to.

In many cases it is possible to change the chemical nature of one of the components in such a way that it can be easily reconverted into the original substance. Insoluble acids (*e. g.*, benzoic and salicylic acids) may be separated from other substances by treatment with caustic soda. The sodium salts of these acids being soluble go into solution which may be separated from the insoluble portion by filtration. The acids may now be precipitated from the solution with dilute sulphuric acid.

Similarly insoluble bases may be dissolved out in dilute hydrochloric acid.

In certain cases the separation can be brought about only by destroying one of the constituents. It

is really no separation. It is the isolation of the one component at the cost of the other.

2. **Separation of a Solid from a Liquid.**—If the solid is insoluble and is present in the form of a precipitate, it may be separated simply by **decantation and filtration.** If the particles are very small and do not show any sign of settling down, they may be made to settle by **centrifugal force.**

If the mixture is in the form of a solution, the solvent may be distilled off. If the boiling point of the liquid is very high and it decomposes at this temperature under ordinary pressures, it may be distilled under **reduced pressure**.

Certain substances are volatile in steam and are separated from the other components by **steam distillation.**

3. **Separation of a Gas from a Solid.**—Such mixtures are not common. When Palladium is heated to 90—97°C in an atmosphere of hydrogen, it takes up hydrogen. It begins to give out the absorbed hydrogen at 100°C. The hydrogen, is also given out when it is cooled down to ordinary temperatures

Ordinary smoke is a suspension of very small particles of carbon in air. When these particles aggregate together they form soot.

4. **Separation of a Liquid from another Liquid.**—The two liquids of a binary mixture may be,

(*a*) immiscible *e g.*, chloroform and water,

(*b*) partially miscible *e g.*, ether and water,

or

(*c*) completely miscible *e. g.*, alcohol and water.

(*a*) When the component liquids are immiscible they may be separated by means of a tap-funnel. The heavier liquid forms the lower layer and may be drawn off through the tap.

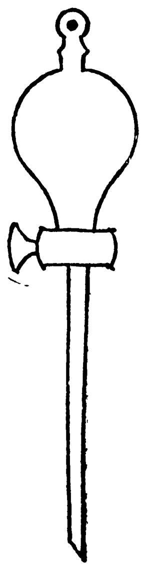


Figure 19.

(*b*) When the mixture contains sufficient quantities of two partially miscible liquids, they will form two layers in a separating funnel. Taking ether and water as an example, the upper layer will be a solution of water in ether and the lower layer a solution

of ether in water. These two layers may be separated by means of the tap-funnel and the two layers may be treated as two different solutions. [See *(c)* below].

(c) When the liquids are completely miscible, they may be separated by **fractional distillation** or some suitable chemical method.

The boiling point of a liquid is that temperature at which the vapour pressure of the liquid is equal to the pressure of the atmosphere. Therefore at a particular temperature the vapour pressure of the higher boiling point liquid is lower than that of the lower boiling point liquid. Now if equal volumes of the two liquids are mixed together, the vapour pressure of the mixture is between those of the two pure liquids and it will begin to boil at a temperature somewhere between the boiling points of the two liquids. The composition of the vapour will depend upon the vapour pressures of the two liquids and also upon their relative proportions. If such a mixture is distilled, the boiling point rises continuously, which shows that there is a constant change in the composition of the liquid in the distilling vessel.

If the distillate is collected in different receivers (say after every five degrees rise of temperature), the first fraction contains a higher proportion of the lower boiling point liquid which goes on decreasing in the successive fractions till the last fraction con-

tains an equaly high proportion of the liquid which boils at the higher temperature. Therefore even in the first distillation (fractionation) a partial separation has been brought about.

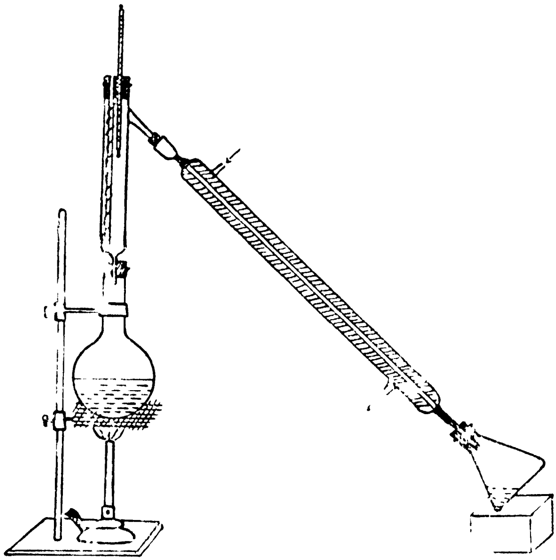


Figure 20.

The operation of fractional distillation is facillated by using a distilling flask with a long neck or more efficiently a **still head** (fractionating column). The increased surface has a cooling effect on the vapours, whereby some of higher boiling point liquid condenses and returns to the distilling vessel. The fractionating column helps in the separation of the two liquids.

When the boiling points of the two liquids are widely apart, a single distillation brings about a more

or less complete separation, but in most cases it is necessary to redistil the fractions. The following example will make it clear.

A mixture of 75 c. c. of benzene (B. P. 80°) and an equal volume of toluene (B. P. 110°) was fractionally distilled in an apparatus as shown in the figure. The fractions were collected as shown in table 1 below.

Table 1.

First Fractionation.

	I	II	III	IV	V
Range of temperature	85°	85-92°	92-98°	98-104°	104-110°
Volume of distillate	39 c.c	30c c.	21c.c.	16c.c.	37c c.

Fraction No. 1 was redistilled from a smaller flask and the distillate was collected in a receiver till the thermometer registered a temperature of 83°C. As soon as the temperature began to rise above 83°, the fraction No. 2 was added and the distillation continued without changing the receiver. The receiver was changed when the temperature was rising above 83°C. A quantity of the distillate was collected in the second receiver till the temperature was 91°C. and the fraction No. III was added without changing the receiver. This was continued till all the five

fractions were distilled in this way. The readings of the second fractionation are given in Table 2. below.

Table 2.

Second Fractionation.

	I	II	III	IV	V
Range of temperature	83°	83-91°	91-97°	97-104°	104-110°
Volume of distillate	45 c.c.	22 c.c	12 c c.	7 c c.	52 c.c.

If the two tables are compared, it will be observed that the two end fractions increase in the volume at the cost of the middle fractions.

The third and the fourth fractionations were carried out and the readings were taken as shown in tables 3 and 4 respectively.

Table 3.

Third Fractionation.

	I	II	III	IV	V
Range of temperature	81°	81-88°	88-98°	98-104°	104-110°
Volume of distillate.	48 c.c	15 c.c.	8 c.c	5 c c.	56 c.c.

Table 4.

Fourth Fractionation.

	I	II	III
Range of temperature	81°	81-104°	104-110°
Volume of distillate	52 c.c.	15 c.c.	62 c c.

The fraction No. 1 may be taken as almost pure benzene and fraction No. III as almost pure toluene.

Fractional distillation is not applicable in all cases of miscible liquids. When the boiling points lie close together or when the liquids form a mixture of a constant boiling point, the components cannot be separated by fractional distillation.

It is sometimes convenient to separate the constituents by chemical means. Acetone and methyl alcohol may be separated from acetic acid (as in pyroligneous acid) by fixing the acid with lime and distilling the mixture. Alcohol and acetone will pass over while the acid will remain in the distilling vessel in the form of its calcium salt, from which the acid may be obtained by distillation with sulphuric acid.

5. Separation of a Gas from a Liquid.—The solubility of a gas in a liquid increases with the increase in the pressure and decreases with rising temperature.

Therefore a gas may be taken out of solution either by reducing the pressure or increasing the temperature. There are some gases the solubility of which increases with the rise in temperature.

Froth or foam is a suspension of the minute bubbles of a gas in a liquid.

The gas may be separated from the liquid by centrifugal force.

Fog and mist are suspensions of minute particles of a liquid in a gas.

6. Separation of a Gas from another Gas.—Gases are miscible in all proportions. They may be sepated by diffusion or by the help of some solvent. Oxygen may be separated from nitrogen by passing through a solution of pyrogallic acid.

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INDEX.

THE END.